88737 Access DB# _____

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: Maurie Baker (BAKER) Examiner #: 16680 Date: 3/10/03
Art Unit: 1639 Phone Number 308-0065 Serial Number: 09/762320
Mail Box and Bldg/Room Location: 3B01 Results Format Preferred (circle): ~~PAPER~~ DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

****

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: _____

Inventors (please provide full names): see attached

Earliest Priority Filing Date: 11/99

***For Sequence Searches Only* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.**

- Please search attached claims.
- Most importantly, search specific compounds of claim 2 & cross with text:

polymer supported, polymeric reagent, solid support, solid supported, resin, bead, solid phase.

- Please also run a separate inventor search.

Thank you!

****

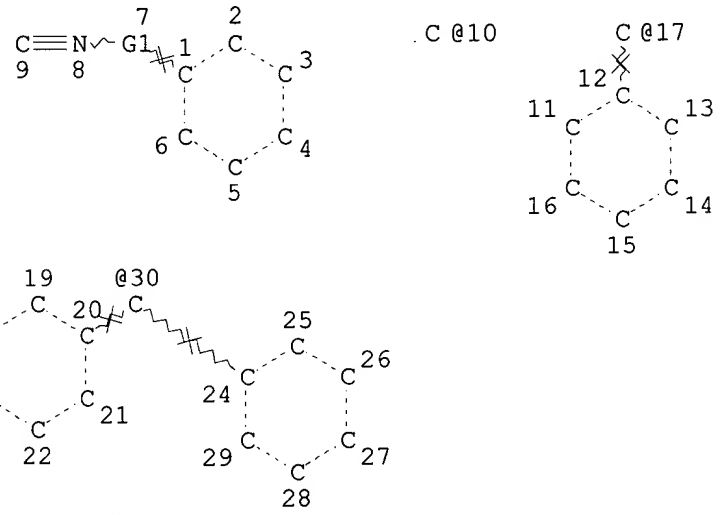
STAFF USE ONLY	Type of Search		Vendors and cost where applicable	
Searcher: Shyamala	NA Sequence (#)		STN	
Searcher Phone #: 308-4559	AA Sequence (#)		Dialog	
Searcher Location:	Structure (#)		Questel/Orbit	
Date Searcher Picked Up:	Bibliographic		Dr.Link	
Date Completed: 3/13/03	Litigation		Lexis/Nexis	
Searcher Prep & Review Time:	Fulltext		Sequence Systems	
Clerical Prep Time:	Patent Family		WWW/Internet	
Online Time:	Other		Other (specify)	

PTO-1590 (1-2000)

```
=> fil hcaplus
FILE 'HCAPLUS' ENTERED AT 11:47:22 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)
```

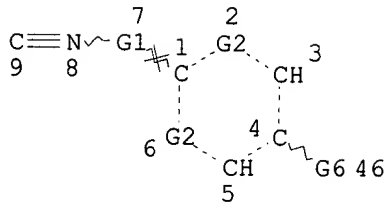


```
FILE COVERS 1907 - 13 Mar 2003  VOL 138 ISS 11
FILE LAST UPDATED: 12 Mar 2003  (20030312/ED)

 This file contains CAS Registry Numbers for easy and accurate
 substance identification.


=>
=>

=> d stat que
L1                STR
```

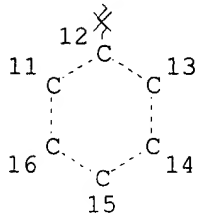



```
VAR G1=10/17/30
NODE ATTRIBUTES:
NSPEC   IS RC     AT  10
NSPEC   IS RC     AT  17
NSPEC   IS RC     AT  30
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS  30

STEREO ATTRIBUTES: NONE
L5         1338 SEA FILE=REGISTRY SSS FUL L1
```

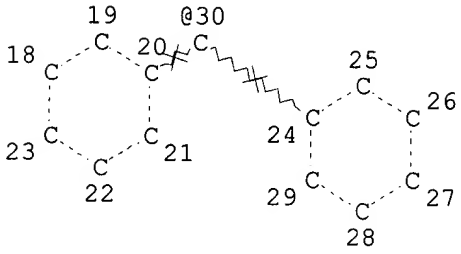
L8 STR



CH2 @10



C~G3
@31 32

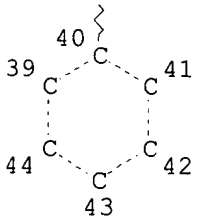


C~G4~CH3
@33 34 35

O~G5~CH3
@36 37 38

O @45

Page 1-A



Page 2-A
VAR G1=10/17/30
VAR G2=CH/31
VAR G3=ME/ET/I-PR/N-PR/I-BU/N-BU/T-BU/S-BU/33/36/45
REP G4=(3-4) C
REP G5=(0-5) C
VAR G6=O/C
NODE ATTRIBUTES:
NSPEC IS RC AT 30
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 46

STEREO ATTRIBUTES: NONE
L9 36 SEA FILE=REGISTRY SUB=L5 SSS FUL L8
L10 37 SEA FILE=HCAPLUS ABB=ON PLU=ON L9

=>

=>

=> d ibib abs hitrn l10 1-37

L10 ANSWER 1 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2002:379191 HCAPLUS
DOCUMENT NUMBER: 137:279443
TITLE: The universal Rink-isonitrile resin: applications in Ugi reactions
AUTHOR(S): Chen, Jack J.; Golebiowski, Adam; Klopfenstein, Sean R.; West, Laura
CORPORATE SOURCE: Combinatorial Chemistry Group, Procter and Gamble Pharmaceuticals, Mason, OH, 45040, USA
SOURCE: Tetrahedron Letters (2002), 43(22), 4083-4085
CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The Rink-isonitrile resin provides a new universal platform for Ugi multi-component reactions. Applications were demonstrated by the traceless synthesis of diketopiperazines, benzodiazepines, and 5-substituted 1H-tetrazoles.
IT **342395-21-5D**, resin-bound
RL: RCT (Reactant); RACT (Reactant or reagent)
(multi-component Ugi reactions for prepn. of heterocyclic compds. using Rink-isonitrile resin and cyclization reaction of linear dipeptides)
REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 2 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:746786 HCAPLUS
DOCUMENT NUMBER: 136:101996
TITLE: Kinetics of solvent addition on electrosprayed ions in an electrospray source and in a quadrupole ion trap
AUTHOR(S): Gabelica, V.; Lemaire, D.; Laprevote, O.; De Pauwa, E.
CORPORATE SOURCE: Bat B6c, Departement de Chimie, Laboratoire de Spectrometrie de Masse, Universite de Liege, Liege, B-4000, Belg.
SOURCE: International Journal of Mass Spectrometry (2001), 210/211(1-3), 113-119
CODEN: IMSPF8; ISSN: 1387-3806
PUBLISHER: Elsevier Science B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Benzylpyridinium cations readily fragment in the electrospray source by loss of pyridine to give benzyl cations (M-79). The full-scan spectra obtained with some instruments also show, in addn., an m/z (M-38) peak corresponding to the addn. of acetonitrile, being present in the solvent mixt., on the benzyl cations. Here we report that the addn. reaction can occur in the source region of electrospray mass spectrometry instruments, and in a quadrupole ion trap. The kinetics of acetonitrile addn. was monitored in an ion trap, acetonitrile being provided by leakage from the source, through the heated capillary. For benzyl ions with different substituents, the addn. kinetics has been found pos. correlated with the Brown parameter .sigma.+ of the benzyl radical, and therefore with the effective charge d. on the .alpha.-carbon atom of the benzyl ion. This is consistent with the Langevin or av.-dipole-orientation (ADO) theory of ion-mol. reaction kinetics.
IT **388596-68-7 388596-84-7**
RL: FMU (Formation, unclassified); FORM (Formation, nonpreparative)
(kinetics of addn. of acetonitrile solvent to electrospray fragment ions in an electrospray source and in a quadrupole ion trap)
REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS

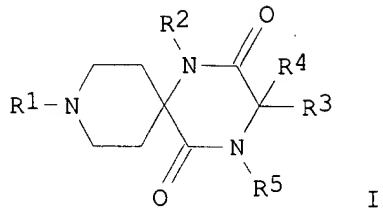
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 3 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:416939 HCAPLUS
DOCUMENT NUMBER: 135:46203
TITLE: Preparation and effect of triazaspiro[5.5]undecane derivatives as active ingredients in remedy for inflammatory diseases
INVENTOR(S): Habashita, Hiromu; Hamano, Shinichi; Shibayam, Shiro; Takaoka, Yoshikazu
PATENT ASSIGNEE(S): Ono Pharmaceutical Co., Ltd., Japan
SOURCE: PCT Int. Appl., 1149 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

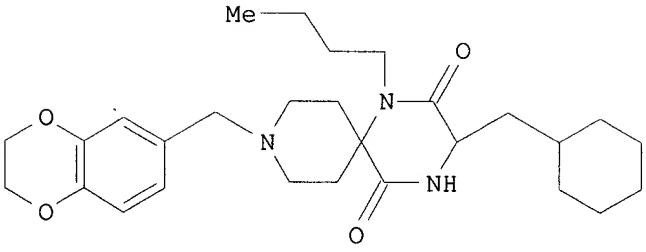
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001040227	A1	20010607	WO 2000-JP8517	20001201
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
AU 2001016506	A5	20010612	AU 2001-16506	20001201
EP 1236726	A1	20020904	EP 2000-979050	20001201
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
NO 2002002609	A	20020726	NO 2002-2609	20020531

PRIORITY APPLN. INFO.:
JP 1999-344967 A 19991203
JP 2000-18673 A 20000127
JP 2000-27968 A 20000204
JP 2000-147882 A 20000519
WO 2000-JP8517 W 20001201

OTHER SOURCE(S): MARPAT 135:46203
GI



I



II

AB Title compds. [I; R1 = H, aryl, arylalkyloxycarbonyl, alkenyloxycarbonyl, heterocyclylalkyl, alkyl, alkenyl, alkynyl; R2 = alkyl, alkynyl; R3 = H; R4 = alkyl; R5 = H, alkyl], stereoisomers, quaternary ammonium salts thereof, N-oxides thereof and nontoxic salts thereof, are prepd. via solid phase synthesis using divinylbenzene-polystyrene or divinylbenzene-Rink resin. Title compds. I, having controlling effects of chemokines/chemokine receptors, are useful in preventing and/or treating various inflammatory diseases, asthma, atopic dermatitis, urticaria, allergic diseases, nephritis, nephropathy, hepatitis, arthritis, rheumatoid arthritis, etc. Thus, the title compd. II.cntdot.HCl was prepd. and biol. tested.

IT **342395-21-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(prepn. and effect of triazaspiro[5.5]undecane derivs. as active ingredients in inflammatory disease therapy)

REFERENCE COUNT: 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 4 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:396735 HCAPLUS
DOCUMENT NUMBER: 135:19230
TITLE: New functionalized polymeric reagents with an isonitrile moiety for solution and solid-phase synthesis
INVENTOR(S): Page, Patrick
PATENT ASSIGNEE(S): Astrazeneca Ab, Swed.
SOURCE: PCT Int. Appl., 33 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE

WO 2001037983 A1 20010531 WO 2000-SE2263 20001116
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
EP 1239949 A1 20020918 EP 2000-981995 20001116
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL
PRIORITY APPLN. INFO.: SE 1999-4222 A 19991122
WO 2000-SE2263 W 20001116
OTHER SOURCE(S): CASREACT 135:19230; MARPAT 135:19230
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to functionalized polymeric reagents useful in soln. and solid-phase synthesis. It relates more specifically to a functionalized polymeric reagent comprising an acid-labile isonitrile moiety. In particular, it relates to reagents I [Ps = polymeric support; X = C, O, PEG chain, or (CH2)nCONH; R1, R2 = H, (un)substituted Ph; R3, R4 = H, C1-6 alkyl or alkoxy, OPh; n = 1-4]. The invention also relates to use of such reagents in soln. and solid-phase synthesis, to a method for prepg. an org. compd. by such use, to a method for prepg. such reagents, and to kits comprising them. The invention also relates to new intermediates, specifically the corresponding formamides II, for use in the prepn. of I. The invention further provides I for use in soln. and solid-phase synthesis, e.g., multicomponent reactions. The functionalized polymeric reagent comprises a linker, and said linker comprises an acid-labile isonitrile moiety. The linker is covalently attached to the polymeric support. For instance, the MAMP amino resin III (comprising support and linker) in DMF was treated with 2,4,5-trichlorophenyl formate, and the resultant N-formylated resin, i.e., II, was washed and treated with PPh3, CCl4, and Et3N, to give the invention reagent IV. The latter was kept under N at room temp., in the dark, for 6 mo without any change in its efficiency. I undergo Ugi (multicomponent) reaction with heteroarom. amidines and aldehydes R6CHO in the presence of catalytic Sc(OTf)3, followed by optional N-acylation, N-alkylation, or N-sulfonylation (with other diversity-adding components), and cleavage from the resin, to give 3-amino[fused]imidazole derivs. V [A = atoms to complete fused heteroarom. ring; R5 and R6 not specified; R7 = RSO2, RCH2, RCO; R not specified; no examples] in high (75-99%) purity. The reagents are suitable for prepn. of combinatorial libraries.

IT **342395-21-5DP**, resin-bound **342773-59-5DP**, resin-bound **342773-60-8DP**, resin-bound **342773-61-9DP**, resin-bound
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(reagent; prepn. of polymer-bound isonitriles as new functionalized polymeric reagents)

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 5 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:177277 HCAPLUS
DOCUMENT NUMBER: 135:46139
TITLE: Universal Rink-isonitrile resin: application for the

traceless synthesis of 3-(acylamino)imidazo[1,2-a]pyridines
AUTHOR(S): Chen, J. J.; Golebiowski, A.; McClenaghan, J.; Klopfenstein, S. R.; West, L.
CORPORATE SOURCE: Combinatorial Chemistry Group, Procter & Gamble Pharmaceuticals, Mason, OH, 45040, USA
SOURCE: Tetrahedron Letters (2001), 42(12), 2269-2271
CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:46139
AB Rink resin was converted to isonitrile resin after formylation with HCO2H/diisopropylcarbodiimide followed by POCl3/diisopropylethylamine dehydration. This polymer-supported isonitrile was then employed in the multi-component synthesis of imidazo[1,2-a]pyridines. The resin-bound imidazo[1,2-a]pyridine was acylated and spontaneously released by acyl chloride treatment in dichloroethane.
IT **344594-17-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(solid-phase synthesis of (acylamino)imidazo[1,2-a]pyridines)
REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 6 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:709811 HCAPLUS
DOCUMENT NUMBER: 132:63776
TITLE: Dramatic solvent effect in the multicomponent reaction of nitro compounds with isocyanides
AUTHOR(S): Dumestre, Paul; El Kaim, Laurent
CORPORATE SOURCE: Laboratoire Reacteurs et Processus, Ecole Nationale Superieure de Techniques avancees, Paris, 75015, Fr.
SOURCE: Tetrahedron Letters (1999), 40(45), 7985-7986
CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 132:63776
AB Nitro compds., triethylamine, acetic anhydride, and isocyanides react together in toluene giving .alpha.-oximino amides in low to moderate yields. Much faster and higher yielding reactions are obtained when DMSO is chosen as solvent.
IT **1197-58-6**
RL: RCT (Reactant); RACT (Reactant or reagent)
(solvent effect in the multicomponent reaction of nitro compds. with isocyanides)
REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 7 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:613947 HCAPLUS
DOCUMENT NUMBER: 131:243287
TITLE: Preparation of dioxopiperazinoacetamides as fructose-1,6-bisphosphatase inhibitors
INVENTOR(S): Mjalli, Adnan M. M.; Mason, James Christopher; Arienti, Kristen Lee; Short, Kevin Michael; Kimmich, Rachel Denise Anne; Jones, Todd Kevin
PATENT ASSIGNEE(S): Ontogen Corporation, USA
SOURCE: PCT Int. Appl., 74 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1

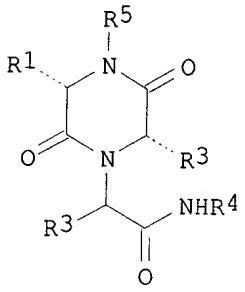
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9947549	A1	19990923	WO 1999-US5552	19990315
W: AU, CA, JP				
RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
AU 9930870	A1	19991011	AU 1999-30870	19990315
US 6107274	A	20000822	US 1999-270121	19990315
EP 1070084	A1	20010124	EP 1999-912505	19990315
R: DE, FR, GB				
JP 2001294586	A2	20011023	JP 2000-386045	19990315

PRIORITY APPLN. INFO.: US 1998-78065P P 19980316
WO 1999-US5552 W 19990315

OTHER SOURCE(S): MARPAT 131:243287

GI



I

AB Title compds. [I; R1 = cycloalkyl or aralkyl; R2 = cycloalkylmethyl or (ar)alkyl; R3 = H, F, alkyl, substituted Ph; R4 = H, alkyl, acyl, substituted Ph; R5 = H; R1R5 = atoms to complete a ring] were prepd. Thus, L-R2CH(NH2)CO2Me.HCl (R2 = cyclohexyl), 4-(NC)C6H4CHO, N-Fmoc-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid, and 4-(CNH2CH2C)C6H4OCH2Ph were subjected to Ugi condensation and the product cyclized to give, after deprotection, I [R1R5 = 2-(H2C)C6H4CH2, R2 = cyclohexylmethyl, R3 = 4-(NC)C6H4, R4 = CH2CH2C6H4(OH)-4]. Data for biol. activity of I were given.

IT **244221-05-4 244221-06-5**
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of dioxopiperazinoacetamides as fructose-1,6-bisphosphatase inhibitors)

REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 8 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:375282 HCAPLUS
DOCUMENT NUMBER: 131:44656
TITLE: Preparation of N-(4-amidinophenyl)phenylglycineamides as factor VIIa/tissue factor inhibitors
INVENTOR(S): Grobke, Katrin; Ji, Yu-hua; Wallbaum, Sabine; Weber, Lutz
PATENT ASSIGNEE(S): F. Hoffmann-La Roche A.-G., Switz.
SOURCE: Eur. Pat. Appl., 46 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1

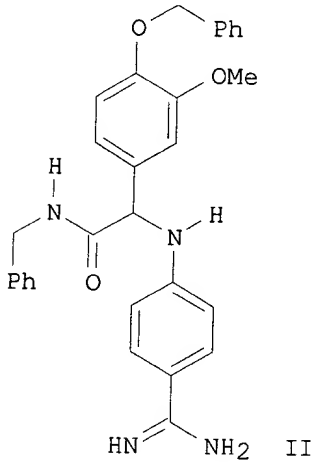
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 921116	A1	19990609	EP 1998-122169	19981126
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
NZ 333126	A	20000623	NZ 1998-333126	19981202
US 6140353	A	20001031	US 1998-204373	19981202
ZA 9811077	A	19990604	ZA 1998-11077	19981203
NO 9805646	A	19990607	NO 1998-5646	19981203
AU 9895210	A1	19990624	AU 1998-95210	19981203
AU 739769	B2	20011018		
MX 9810201	A	20000831	MX 1998-10201	19981203
CN 1224714	A	19990804	CN 1998-126979	19981204
JP 11246507	A2	19990914	JP 1998-345875	19981204
JP 3236267	B2	20011210		
BR 9805320	A	20000411	BR 1998-5320	19981204

PRIORITY APPLN. INFO.: EP 1997-121285 A 19971204
EP 1998-121374 A 19981110

OTHER SOURCE(S): MARPAT 131:44656

GI



II

AB RR1NCOCHR2NHZC(:NG1)NHG2 [I; 1 of G1,G2 = H and the other = H, OH, alkyl, alkoxy, etc.; R = (un)substituted alkyl, cycloalkyl, aryl; R1 = H or alkyl; R2 = (un)substituted Ph or -pyridyl; Z = (3-hydroxy) 1,4-phenylene] were prepd. Thus, 3,4-(MeO)(PhCH2O)C6H3CHO, 4-(H2N)C6H4C(:NH)NH2, and PhCH2NC were condensed to give, after acidification, title compd. II.HCl. Data for biol. activity of I were given.

IT **1197-58-6**, 4-Methoxybenzyl isocyanide
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of N-(4-amidinophenyl)phenylglycineamides as factor VIIa/tissue factor inhibitors)

REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 9 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:300786 HCAPLUS
DOCUMENT NUMBER: 131:87685
TITLE: Chiral 1,3-diamines from a lithiated isocyanide and chiral aziridines
AUTHOR(S): Kaiser, Alexander; Balbi, Miriam

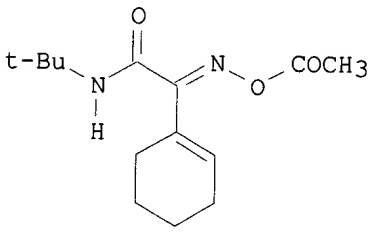
CORPORATE SOURCE: Institut Pharmazie, Pharmazeutische Chemie I, Universitat Regensburg, Regensburg, D-93040, Germany
SOURCE: Tetrahedron: Asymmetry (1999), 10(5), 1001-1014
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 131:87685

AB Reaction of lithiated 4-methoxybenzyl isocyanide with homochiral amino acid derived N-tosyl- and N-diphenylphosphinoylaziridines proceeds diastereoselectively to provide N-protected 3-isocyanoamines. Sepn. of the diastereomers of these adducts or the corresponding formamides, and subsequent transformations, lead to 1,3-diamines and their mono-protected and differentially bis-protected derivs.

IT **1197-58-6**
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of chiral 1,3-diamines from lithiated isocyanide and chiral aziridines)

REFERENCE COUNT: 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 10 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:273634 HCAPLUS
DOCUMENT NUMBER: 131:115835
TITLE: A new multicomponent reaction of nitro compounds with isocyanides
AUTHOR(S): Dumestre, Paul; Kaim, Laurent El; Gregoire, Ariane
CORPORATE SOURCE: Laboratoire Reacteur et Processus, Ecole Nationale Superieure de Techniques Avancees, Paris, 75015, Fr.
SOURCE: Chemical Communications (Cambridge) (1999), (9), 775-776
CODEN: CHCOFS; ISSN: 1359-7345
PUBLISHER: Royal Society of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 131:115835
GI



I

AB The first multicomponent reaction between nitro compds., isocyanides and acylating agents is described, providing an original route to .alpha.-oximinoamides. Thus, reaction of 1-(nitromethyl)-1-cyclohexene with Me3CNC and Ac2O gave adduct I in 63% yield.

IT **1197-58-6**
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of .alpha.-oximinoamides via multicomponent addn. reactions of nitro compds. with isocyanides)

REFERENCE COUNT: 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 11 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1998:269825 HCAPLUS

DOCUMENT NUMBER: 129:45739
TITLE: Studies of the Adsorption of Bi- and Tridentate Isocyanides on Gold Powder
AUTHOR(S): Ontko, Allyn C.; Angelici, Robert J.
CORPORATE SOURCE: Department of Chemistry, Iowa State University, Ames, IA, 50011, USA
SOURCE: Langmuir (1998), 14(11), 3071-3078
CODEN: LANGD5; ISSN: 0743-7463
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Diffuse reflectance Fourier transform spectroscopy (DRIFTS) studies of diisocyanides [C.tplbond.N-(CH2)x-N.tplbond.C, where x = 2, 4, 6, 8, and 12; m- and p-xylyl(NC)2, xylyl = -CH2-C6H4-CH2-] and triisocyanides [1,1,1-tris(isocyanomethyl)ethane (Tripod(NC)3) and tris[2-isocyanoethyl]amine (Tren(NC)3)] adsorbed on gold (Au) powder show that all of their -NC groups are coordinated to the surface. The .nu.(NC) values (cm-1) for the adsorbed ligands are .apprx.2220 cm-1, which indicates that each of the -NC groups is bound through the carbon to a single Au atom. The satn. coverages (n1s) for the diisocyanides decrease as the linking -(CH2)x- group lengthens from x = 2 to x = 12. At satn. coverage, the no. of moles of -N.tplbond.C groups coordinated for C12(NC)2 is similar to that for the monoisocyanide n-C18H37NC, whereas twice as many -NC groups are adsorbed for C2(NC)2 than n-C18H37NC. Qual. kinetic measurements show that all of the monoisocyanide n-C18H37NC adsorbed on Au powder is displaced by C4(NC)2 within 90 min. However, only 39% of the diisocyanide m-xylyl(N13C)2 is displaced by C4(NC)2, even after 120 h, demonstrating that only 34-39% of the diisocyanide m-xylyl(N13C)2 is exchangeable and the remaining 61-66% of the diisocyanide is kinetically inert to exchange. The existence of two adsorption regimes, low coverage (>61-66%) and high coverage (above 61-66%), on the Au powder is supported by a variety of evidence. Reaction quotients (Qab), which probably include both kinetic and thermodn. factors, for the adsorption of diisocyanides on Au increase significantly as the -(CH2)x- link between the -NC groups becomes shorter. The C2(NC)2 ligand has the highest Qab value. These studies also show that the relative binding affinities of the isocyanides increase as the no. of -NC groups in the ligand increases (RNC < R(NC)2 < R(NC)3).

IT **4973-73-3P**
RL: PEP (Physical, engineering or chemical process); PRP (Properties); SPN (Synthetic preparation); PREP (Preparation); PROC (Process)
(adsorption of bi- and tridentate isocyanides on gold powder)

REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 12 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1998:74145 HCAPLUS
DOCUMENT NUMBER: 128:140349
TITLE: Thermal Isomerizations of Substituted Benzyl Isocyanides: Relative Rates Controlled Entirely by Differences in Entropies of Activation
AUTHOR(S): Kim, Sung Soo; Choi, Won Jung; Zhu, Yu; Kim, Jin Hyun
CORPORATE SOURCE: Department of Chemistry and Center for Molecular Dynamics, Inha University, Inchon, 402-751, S. Korea
SOURCE: Journal of Organic Chemistry (1998), 63(4), 1185-1189
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The abs. and relative rates of thermal rearrangements of substituted benzyl isocyanides were obtained at the temps. between 170 and 230.degree.. The relative rates are independent of temp. and exhibit excellent Hammett correlations (.rho.+ = 0.24). The temp. studies yielded

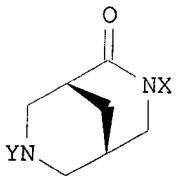
activation parameters (.DELTA.HY.thermod. and .DELTA.SY.thermod.) and their differential counterparts (.DELTA..DELTA.HY-H.thermod. and .DELTA..DELTA.SY-H.thermod.). The differential terms were plotted against .sigma.+. The secondary .alpha.-deuterium kinetic isotope effects (kD/kH = 1.11) were measured at several temps. The rate data can be rationalized with the cyclic TS. The substituent effects on the rates are due to the entropic contributions.

IT **1197-58-6**, 4-Methoxybenzyl isocyanide
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(thermal isomerizations of substituted benzyl isocyanides)

L10 ANSWER 13 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1997:654833 HCAPLUS
DOCUMENT NUMBER: 127:293136
TITLE: Preparation of diazabicyclo[3.3.1]nonanes as drugs
INVENTOR(S): Inaba, Takayuki; Abe, Hiroyuki; Miyazaki, Susumu
PATENT ASSIGNEE(S): Japan Tobacco, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 21 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 09255679	A2	19970930	JP 1996-66860	19960322

PRIORITY APPLN. INFO.: JP 1996-66860 19960322
OTHER SOURCE(S): CASREACT 127:293136; MARPAT 127:293136
GI



I

AB The title compds. [I; X = H, R; Y = H, C6H5CH2; R = CONH(CHR1)mR2, COR3, etc.; R1 = H, alkyl; R2 = (un)substituted aryl or cycloalkyl, etc.; R3 = alkyl, aralkyloxy] are prepd. from 3-bromo-5-carboxypyridine by esterification, cyanation, hydrogenation, cyclization, optical resoln., etc. I are useful as nicotine cholinergic agents for prevention and treatment of Alzheimer diseases, dementia diseases, memory disorder, central neurodegenerative diseases, brain disfunction, and related diseases (no data). Thus, I (X = H, Y = C6H5CH2) (prepn. given) was reacted with p-MeOC6H4CH2NCO and hydrogenated over Pd/C to give the title compd. I (Y = H, X = p-MeOC6H4CH2NHCO).

IT **1197-58-6**, 4-Methoxybenzyl isocyanide
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of diazabicyclo[3.3.1]nonanes as drugs)

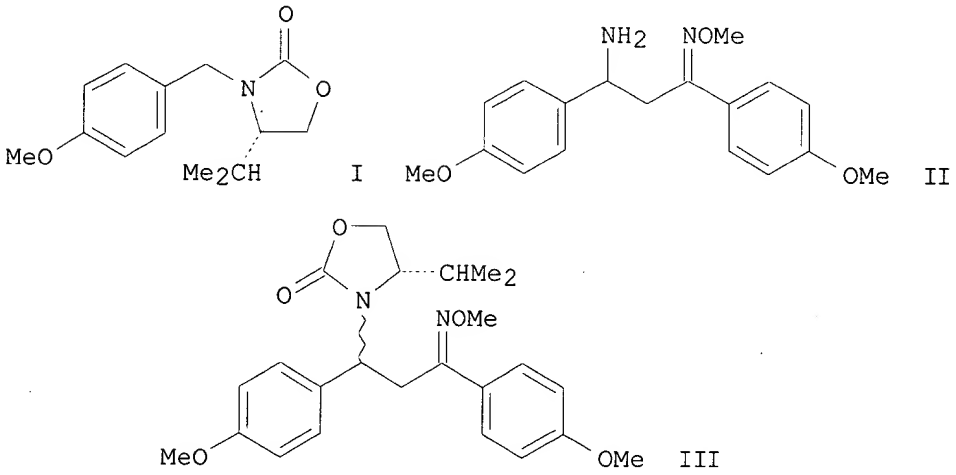
L10 ANSWER 14 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1996:684938 HCAPLUS
DOCUMENT NUMBER: 126:18629
TITLE: 1,3-Diphenylpropane-1,3-diamines. Part IX. Reaction of

.alpha.-chloro oxime ethers with .alpha.-lithiobenzylamines

AUTHOR(S): Kaiser, A.; Wiegrebe, W.
CORPORATE SOURCE: Inst. Pharmacy, Univ. Regensburg, Regensburg, D-93040, Germany

SOURCE: Monatshefte fuer Chemie (1996), 127(6/7), 763-774
CODEN: MOCMB7; ISSN: 0026-9247
PUBLISHER: Springer
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 126:18629

GI



AB The carbanions of the benzylamine derivs. 4-MeOC6H4CH2NC, 4-MeOC6H4CH2NHCOPh, isoxazolidine I, and 4-MeOC6H4CH2NCHC6H4-4-OMe were reacted with 4-MeOC6H4C(CH2Cl)NOMe to get precursors of 1,3-diphenylpropane-1,3-diamines. Isonitrile 4-MeOC6H4CH2NC afforded the expected result, whereas lithiated benzamide 4-MeOC6H4CH2NHCOPh underwent oxidative dimerization and transmetallated 4-MeOC6H4C(CH2Cl)NOMe. Isoxazolidine I gave the condensation product II as a mixt. of diastereomers. Treatment of imine 4-MeOC6H4CH2NCHC6H4-4-OMe led to the desired amino oxime III in low yield.

IT **1197-58-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(prepn. of diphenylpropanediamines from chloro oxime ethers and lithiobenzylamines)

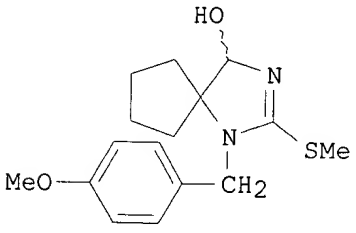
L10 ANSWER 15 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1996:513739 HCAPLUS
DOCUMENT NUMBER: 125:157765
TITLE: 3-Phenyl-Substituted Imidazo[1,5-a]quinoxalin-4-ones and Imidazo[1,5-a]quinoxaline Ureas That Have High Affinity at the GABAA/Benzodiazepine Receptor Complex
AUTHOR(S): Jacobsen, E. Jon; Stelzer, Lindsay S.; Belonga, Kenneth L.; Carter, Donald B.; Im, Wha Bin; Sethy, Vimala H.; Tang, Andrew H.; VonVoigtlander, Philip F.; Petke, James D.
CORPORATE SOURCE: Department of Structural and Medicinal Chemistry, Pharmacia Upjohn, Kalamazoo, MI, 49001, USA
SOURCE: Journal of Medicinal Chemistry (1996), 39(19), 3820-3836

CODEN: JMCMAR; ISSN: 0022-2623
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 125:157765

AB A series of imidazo[1,5-a]quinoxalin-4-ones and imidazo[1,5-a]quinoxaline ureas contg. substituted Ph groups at the 3-position was developed. Compds. within the imidazo[1,5-a]quinoxaline urea series had high affinity for the GABAA/benzodiazepine receptor complex with varying in vitro efficacy, although most analogs were partial agonists as indicated by [35S]TBPS and Cl- current ratios. Interestingly, a subseries of piperazine ureas was identified which had biphasic efficacy, becoming more antagonistic with increasing concn. Analogs within the imidazo[1,5-a]quinoxalin-4-one series had substantially decreased binding affinity as compared to the quinoxaline urea series. These compds. ranged from antagonists to full agonists by in vitro anal., with several derivs. having roughly 4-fold greater intrinsic activity than diazepam as indicated by Cl- current measurement. Numerous compds. from both series were effective in antagonizing metrazole-induced seizures, consistent with anticonvulsant properties and possible anxiolytic activity. Most of the quinoxaline ureas and quinoxalin-4-ones were active in an acute electroshock phys. dependence side effect assay in mice precluding further development.

IT **1197-58-6P**, 4-Methoxybenzyl isocyanide
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate; prepn. of 3-phenyl-substituted imidazo[1,5-a]quinoxalin-4-ones and imidazo[1,5-a]quinoxaline ureas with high affinity at the GABAA/benzodiazepine receptor complex)

L10 ANSWER 16 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1996:440883 HCAPLUS
DOCUMENT NUMBER: 125:195502
TITLE: Preparation of Spiro Hydroxy S-Methylisothioureas from Cyclic Ketones
AUTHOR(S): McAlpine, Indrawan J.; Armstrong, Robert W.
CORPORATE SOURCE: Department of Chemistry and Biochemistry, University of California, Los Angeles, CA, 90095, USA
SOURCE: Journal of Organic Chemistry (1996), 61(16), 5674-5676
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



I

AB Using the Ugi four component condensation 2-thiohydantoin-4-imide synthesis, the authors show the conversion of cyclopentanone to the spirohydroxy-S-methylisothiourea I (R = 4-MeOC6H4CH2). The redn. of 2-thiohydantoin-4-imides can be controlled by selecting an appropriate isocyanide in the Ugi condensation.

IT **1197-58-6**, 4-Methoxybenzyl isocyanide

RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of spiro hydroxy S-methylisothioureas from cyclic ketones)

L10 ANSWER 17 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1996:369154 HCAPLUS
DOCUMENT NUMBER: 125:32963
TITLE: Cyanide Abstractions from Benzyl Isocyanides by Phenyl and Tri-n-Butyltin Radicals: New Examples of SH2 Reactions
AUTHOR(S): Kim, Sung Soo; Yang, Ki Woong; Lee, Chang Soo
CORPORATE SOURCE: Department of Chemistry, Inha University, Incheon, 402-751, S. Korea
SOURCE: Journal of Organic Chemistry (1996), 61(14), 4827-4829
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The abstraction of cyanide from benzyl isocyanides by Ph and tributyltin radicals was studied. Relative rates, Hammet .sigma.-consts. and secondary .alpha.-deuterium kinetic isotope effects were reported.
IT **130287-23-9**, Benzonitrile 4-(isocyanomethyl)
RL: RCT (Reactant); RACT (Reactant or reagent)
(cyano group abstraction from benzyl isocyanides by Ph and tributyltin radicals and examples of SNH2 reactions)

L10 ANSWER 18 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1995:665438 HCAPLUS
DOCUMENT NUMBER: 123:78638
TITLE: Novel Hexakis(areneisonitrile)technetium(I) Complexes as Radioligands Targeted to the Multidrug Resistance P-Glycoprotein
AUTHOR(S): Herman, Lee W.; Sharma, Vijay; Kronauge, James F.; Barbarics, Eva; Herman, Lisa A.; Piwnica-Worms, David
CORPORATE SOURCE: Medical School, Washington University, St. Louis, MO, 63110, USA
SOURCE: Journal of Medicinal Chemistry (1995), 38(15), 2955-63
CODEN: JMCMAR; ISSN: 0022-2623
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Transport substrates and modulators of the human multidrug resistance (MDR1) P-glycoprotein (Pgp) are generally lipophilic cationic compds., many with substituted aryl moieties. We sought to synthesize arom. technetium-isonitrile complexes to enable functional detection in vivo of Pgp expression in tissues. A series of substituted arom. isonitrile analogs were synthesized from their corresponding amines by reaction with dichlorocarbene under phase transfer-catalyzed conditions, and the non-carrier-added hexakis(areneisonitrile)Tc-99m(I) complexes were produced by reaction with pertechnetate in the presence of sodium dithionite. Cellular accumulation in vitro, whole body biodistribution, and the imaging properties of these lipophilic, monocationic organometallic complexes were detd. in Chinese hamster lung fibroblasts expressing MDR Pgp in normal rats, and in rabbits, resp. For this initial series, verapamil (50 .mu.M), the classical Pgp modulator, significantly enhanced cellular accumulation or displaced binding of Tc complexes of 1b, 1d, 1h, 2a, 2d, 3a, and 3b, indicative of targeted interactions with Pgp. Most complexes, despite their modestly high lipophilicity, were excluded by the blood/brain barrier, and several complexes displayed simultaneously high hepatobiliary and renal excretion in vivo, consistent with the physiol. expression pattern of Pgp in these tissues. Selected Tc- and Re-areneisonitrile complexes of this class have potential applicability to the functional imaging and modulation, resp., of MDR Pgp in human tissues.
IT **1197-58-6P**

RL: BAC (Biological activity or effector, except adverse); BPR (Biological process); BSU (Biological study, unclassified); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); PROC (Process); USES (Uses)
(novel hexakis(areneisonitrile)technetium(I) complexes for imaging of multidrug resistance P-glycoprotein)

IT **165459-89-2P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(novel hexakis(areneisonitrile)technetium(I) complexes for imaging of multidrug resistance P-glycoprotein)

L10 ANSWER 19 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1995:137928 HCAPLUS
DOCUMENT NUMBER: 122:105352
TITLE: A convenient preparation of 4-vinylphenylacetic acid and its methyl ester
AUTHOR(S): Wright, Stephen W.; McClure, Lester D.
CORPORATE SOURCE: Pfizer Central Research, Groton, CT, 06340, USA
SOURCE: Organic Preparations and Procedures International (1994), 26(5), 602-5
CODEN: OPPIAK; ISSN: 0030-4948
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 122:105352

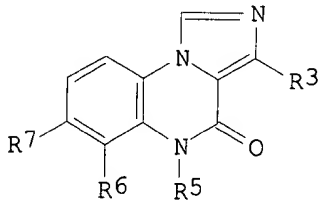
AB The title compds. are prepd. from 4-vinylbenzyl chloride (I), a cheap and isomerically pure starting material. I, KCN, and dicyclohexyl-18-crown-6 in MeCN gives 4-vinylphenylacetonitrile (II) quant. II is hydrolyzed in EtOH/KOH contg. hydroquinone (polymn. inhibitor) to give 95% 4-vinylphenylacetic acid (III). III is esterified with Me2SO4 and KHCO3 in MEK to give 87% Me 4-vinylphenylacetate (IV). The conversion of I directly to 41% IV via Fe(CO)5 mediated 1-step carbonylation with CO is precluded for large scale work due to safety and environmental concerns.

IT **160654-51-3P**
RL: BYP (Byproduct); PREP (Preparation)
(prepn. of 4-vinylphenylacetic acid and Me ester)

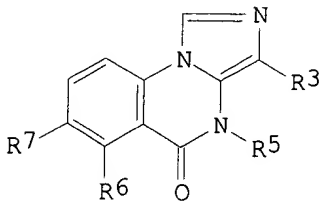
L10 ANSWER 20 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1994:134524 HCAPLUS
DOCUMENT NUMBER: 120:134524
TITLE: 3-Substituted imidazo[1,5-a]quinoxalines and -quinazolines with central nervous system activity
INVENTOR(S): Ten Brink, Ruth Elizabeth; Jacobsen, Eric Jon; Hester, Jackson B., Jr.; Skaletzky, Louis L.
PATENT ASSIGNEE(S): Upjohn Co., USA
SOURCE: PCT Int. Appl., 43 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9317025	A1	19930902	WO 1993-US291	19930125
W: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG				
AU 9334434	A1	19930913	AU 1993-34434	19930125
EP 626966	A1	19941207	EP 1993-903088	19930125
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LI, LU, MC, NL, PT, SE				

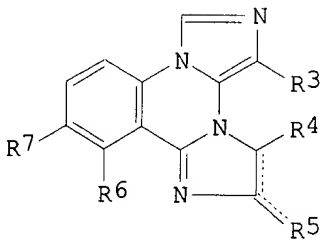
JP 07503970 T2 19950427 JP 1993-514826 19930125
PRIORITY APPLN. INFO.: US 1992-838519 19920219
WO 1993-US291 19930125
OTHER SOURCE(S): MARPAT 120:134524
GI



I



II

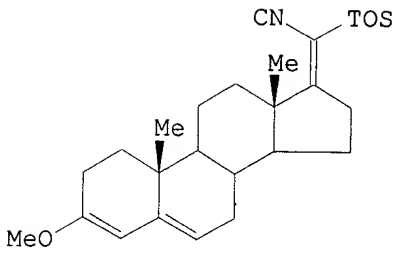


III

AB The title compds. I-III [R3 = (un)substituted heterocyclyl, aryl, arylcarbonyl, etc.; R5 = C1-8 alkyl, C3-7 cycloalkyl, (un)substituted C2-6 alkenyl, etc.; R6, R7 = H, F, Cl, Br, iodo, C1-4 alkyl, CN, NO2, etc.], useful for treating central nervous system disorders assocd. with benzodiazepine receptors (no data), are prepd. Thus, 1,2,3,4-tetrahydro-1-isopropyl-2,3-dioxoquinoxaline was reacted with KOCMe3, di-Et chlorophosphate, and 4-methoxybenzyl isocyanide, producing 4,5-dihydro-5-isopropyl-3-(4-methoxyphenyl)-4-oxoimidazo[1,5-a]quinoxalinane, m.p. 187-189.degree..

IT **1197-58-6**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, in prepn. of agents with central nervous system activity)

L10 ANSWER 21 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1992:84002 HCAPLUS
DOCUMENT NUMBER: 116:84002
TITLE: Chemistry of sulfonylmethyl isocyanides. 33. Synthesis of 17-(isocyanotosylmethylene) steroids: precursors to pregnane derivatives
AUTHOR(S): Van Leusen, Daan; Van Leusen, Albert M.
CORPORATE SOURCE: Dep. Org. Chem., Groningen Univ., Groningen, 9747 AG, Neth.
SOURCE: Recueil des Travaux Chimiques des Pays-Bas (1991), 110(10), 393-401
CODEN: RTCPA3; ISSN: 0165-0513
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 116:84002
GI



I

AB The title steroids, e.g., I were prepd. by reaction of 4-MeC6H4CH2NC with the corresponding 17-oxo steroid.

IT **1197-58-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(prepn. and condensation of, with oxo steroids)

L10 ANSWER 22 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1990:611059 HCAPLUS
DOCUMENT NUMBER: 113:211059
TITLE: Secondary .alpha.-deuterium kinetic isotope effects for addition of phenyl radical to benzyl isocyanides: an evidence of concerted mechanism
AUTHOR(S): Kim, Sung Soo; Lee, Ki Seung; Hwang, Soo Bong; Kim, Hee Jin
CORPORATE SOURCE: Dep. Chem., Inha Univ., Incheon, 402-751, S. Korea
SOURCE: Tetrahedron Letters (1990), 31(25), 3575-8
CODEN: TELEAY; ISSN: 0040-4039
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Addn. of Ph radical to benzyl isocyanides gives benzonitrile and benzyl radicals, exhibiting pos. Hammett .rho. = 0.26 and notable secondary .alpha.-deuterium kinetic isotope effects. These can be rationalized by concerted bond formation/cleavage occurring with polar transition states (TS).
IT **1197-58-6 39495-97-1 130287-23-9**
RL: PRP (Properties)
(addn. of Ph radical to, kinetics and mechanism of)

L10 ANSWER 23 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1987:155575 HCAPLUS
DOCUMENT NUMBER: 106:155575
TITLE: Synthetic potential of the isocyanide-cyanide rearrangement
AUTHOR(S): Meier, Michael; Ruechardt, Christoph
CORPORATE SOURCE: Inst. Org. Chem. Biochem., Univ. Freiburg, Freiburg, D-7800, Fed. Rep. Ger.
SOURCE: Chemische Berichte (1987), 120(1), 1-4
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 106:155575
AB Excellent chem. and optical yields (>96% retention) of cyanides are achieved by vapor phase thermolysis or short contact flow thermolysis of isocyanides. trans-2-Butenyl isocyanide rearranges without concomitant allylic isomerization to trans-2-butenyl cyanide. Optically active PhCH2CH(CN)CH2OCHO is obtained from optically active L-phenylalanine as a new type of chiral pool synthon.
IT **1197-58-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)
(prepn. and thermal rearrangement of)

L10 ANSWER 24 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1987:101575 HCAPLUS
DOCUMENT NUMBER: 106:101575
TITLE: The isonitrile-nitrile rearrangement. A reaction without a structure-reactivity relationship
AUTHOR(S): Meier, Michael; Mueller, Barbara; Ruechardt, Christoph
CORPORATE SOURCE: Inst. Org. Chem. Biochem., Univ. Freiburg, Freiburg, D-7800, Fed. Rep. Ger.
SOURCE: Journal of Organic Chemistry (1987), 52(4), 648-52
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 106:101575

AB Reproducible isomerization rates of aliph. isonitriles to nitriles in soln. were measured by gas-liq. chromatog. or IR spectrometry when free-radical inhibitors are added to suppress a competing radical-chain reaction. The reactivities of 19 primary, secondary, tertiary, cyclic, bicyclic, bridgehead, benzyl, substituted-benzyl, .alpha.-carbomethoxymethyl, and triphenylmethyl isocyanides in this rearrangement reaction vary by only a factor of 67 in rate or by .+-.2 kcal mol-1 in .DELTA.G.thermod.. This is explained by a tight, hypervalent, 3-membered cyclic transition state, in agreement with a previous prediction by ab initio calcn. The slower rate of 9-tripticyl isocyanide is due to steric hindrance by the 3 peri H atoms. Arom. isocyanides isomerize .apprx.10 times faster, independent of polar para substituents and bulky ortho substituents. A hypervalent orthogonal transition state with retention of the arom. sextet is proposed, in contrast to the popular phenonium-type transition states for aryl migration in other 1,2-rearrangements. The reactivity data and transition-state structures are discussed in context with other cationotropic 1,2-shifts.

IT **1197-58-6**
RL: PRP (Properties); RCT (Reactant); RACT (Reactant or reagent)
(rearrangement of, kinetics of)

L10 ANSWER 25 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1982:527638 HCAPLUS
DOCUMENT NUMBER: 97:127638
TITLE: 1-(1,3-Dioxolan-2-ylmethyl)azoles, their salts and their use
INVENTOR(S): Blume, Ernst; Schaper, Wolfgang; Raether, Wolfgang; Dittmar, Walter
PATENT ASSIGNEE(S): Hoechst A.-G. , Fed. Rep. Ger.
SOURCE: Eur. Pat. Appl., 99 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 50298	A2	19820428	EP 1981-108273	19811013
EP 50298	A3	19820818		
R: AT, BE, CH, DE, FR, GB, IT, NL				
DE 3039087	A1	19820519	DE 1980-3039087	19801016
US 4391805	A	19830705	US 1981-311184	19811014

PRIORITY APPLN. INFO.: DE 1980-3039087 19801016
OTHER SOURCE(S): CASREACT 97:127638
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The title azoles I [X = N, CH; Rn = halo, CF3, C1-8 alkyl, C1-4 alkoxy, C3-5 alkenyl, C1-4 alkoxycarbonyl, CO2H, dialkylaminomethyl, NO2, CH:CHCH:CH, (un)substituted PhO; n = 0-3; R1 = H, C1-4 alkyl, (un)substituted Ph; n = 0-2; R2 = (un)substituted NH2 or 1-piperazinyl, R2 = N-contg. heterocyclyl, isocyano, isothiocyanato, NHC(:Z)Z1rR3 [Z = O, S; Z1 = O, NH; r = 0, 1; R3 = H, C1-4 alkyl, halomethyl, (un)substituted Ph]; R4 = naphthyl, halothienyl, Ph], their stereoisomers and salts with physiol. tolerable acids, useful as bactericides, fungicides, and protozoacides (no data), were prepd. Mannich reaction of 4,2-Cl(Me2NCH2)C6H3OH with piperidine gave phenol II which was added to NaH in DMF at .ltoreq.20.degree. and the mixt. treated with cis-dioxolanylmethyl methanesulfonate III to give 86% cis-IV.

IT **82966-03-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

L10 ANSWER 26 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1981:496698 HCAPLUS
DOCUMENT NUMBER: 95:96698
TITLE: Spectroscopic study of the structures of [M2(.eta.-C5H5)2(CO)n(CNR)4n] complexes (n = 1 or 2; M = Fe or Ru) in solution. The structure of cis-[(.eta.-C5H5)(OC)Fe(.mu.-CO)(.mu.-CNCHMe2)Fe(CNCHMe2)(.eta.-C5H5)] in the solid state
AUTHOR(S): Ennis, Mary; Kumar, Rajesh; Manning, Anthony R.; Howell, James A. S.; Mathur, Pradeep; Rowan, Anthony J.; Stephens, Frederic S.
CORPORATE SOURCE: Dep. Chem., Univ. Coll., Dublin, 4, Ire.
SOURCE: Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1981), (6), 1251-9
CODEN: JCDTBI; ISSN: 0300-9246
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Complexes M2L2(CO)n(CNR)4-n were prepd. [L = .eta.-cyclopentadienyl; n = 2, M = Fe, R = Ph, p-ClC6H4CH2, PhCH2, p-MeC6H4CH2, p-MeOC6H4CH2, D-(+)-PhMeCH, Me, Et, Pr, Bu, CHMe2, cyclohexyl, CMe3; M = Ru, R = CHMe2; n = 1, M = Fe, R = Me, Et, CHMe2] and studied by IR and NMR spectroscopy. In soln. they exist as rapidly interconverting equil. mixts. of isomers; where n = 2, the RNC ligands are less likely to adopt bridged as opposed to terminal coordination as R is varied along the above series. The isomer distribution is a consequence of electron-withdrawing R favoring .mu.-CNR coordination and, less importantly, the more bulky R favoring terminal CNR. Where n = 1, only 1 predominant isomer exists in soln. The crystal and mol. structure of cis-Fe2L2(CO)(CNR)(.mu.-CO)(.mu.-CNR) (R = CHMe2) was detd. by x-ray diffraction.

IT **78618-59-4P 78618-61-8P 78656-47-0P**
78656-49-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

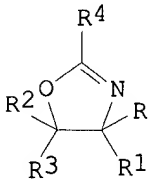
L10 ANSWER 27 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1977:54792 HCAPLUS
DOCUMENT NUMBER: 86:54792
TITLE: Association reactions of tetrakis(arylisonitrile)cobalt(II), rhodium(I) and rhodium(III) complexes in solution
AUTHOR(S): Baumann, D.; Keller, H. J.; Noethe, D.; Rupp, H. H.; Uhlmann, Gerd

CORPORATE SOURCE: Anorg.-Chem. Inst., Univ. Heidelberg, Heidelberg, Fed. Rep. Ger.
SOURCE: Zeitschrift fuer Naturforschung, Teil B: Anorganische Chemie, Organische Chemie (1976), 31B(7), 912-21
CODEN: ZNBAD2; ISSN: 0340-5087
DOCUMENT TYPE: Journal
LANGUAGE: German

AB Investigations on several tetrakis(aryl isonitrile)metal complexes of general stoichiometry M(CNR)4n+ X-n [M = Rh(I), n = 1; M = Rh(III), n = 3; M = Co(II), n = 2; R = Ph, p-tolyl, 4-O2NC6H4, etc.; X = iodide, BPh4, etc.] are described. The paramagnetic complexes of stoichiometry Co(CNR)4I2 dimerize in org. solvents to yield binuclear diamagnetic cations with linear iodide bridges. The amt. of assocn. depends on the iodide content and on exptl. parameters like temp. and/or concn. and can be followed by ir, ESR, and/or NMR techniques. Treating these compds. with ions X- = ClO4- or BPh4 gives the binuclear and diamagnetic complexes of stoichiometry [I-Co(CNR)4-I-Co(CNR)4I]X. The corresponding isonitrile compds. of Rh(I) assoc. in soln. to yield linear stacks in the crystals, the solid state properties of which depend strongly on the type of ligand and the counter anion and vary considerably with the conditions of crystn. The Rh(I) species are able to react with the corresponding tetrakis(arylisonitrile)Rh(III) complexes to give mixeds valence complexes.

IT **61770-66-9P**
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and crystalline properties of)

L10 ANSWER 28 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1976:121700 HCAPLUS
DOCUMENT NUMBER: 84:121700
TITLE: Syntheses with .alpha.-metalated isocyanides, XXXI. 2-Oxazolines from .alpha.-metalated isocyanides and carbonyl compounds. A new synthesis of .beta.-amino alcohols
AUTHOR(S): Schoellkopf, Ulrich; Gerhart, Fritz; Hoppe, Inga; Harms, Ruediger; Hantke, Kurt; Scheunemann, Karl D.; Eilers, Eberhard; Blume, Ernst
CORPORATE SOURCE: Org.-Chem. Inst., Univ. Goettingen, Goettingen, Fed. Rep. Ger.
SOURCE: Justus Liebigs Annalen der Chemie (1976), (1), 183-202
CODEN: JLACBF; ISSN: 0075-4617
DOCUMENT TYPE: Journal
LANGUAGE: German
GI



II, R^4=M
III, R^4=H

AB .alpha.-Metalated isocyanides MCRR1NC [R = H, Me, Ph; R1 = H, Me, Ph, 4-MeOC6H4, pyridyl, PhS, PhCH2S, 4-MeC6H4S; RR1 = (CH2)2, (CH2)5 M = Li, K], prepd. from HCRR1NC and BuLi, KOCMe3, or Li tetramethylpiperidide in THF, reacted at .apprx.-70.degree. with carbonyl compds. R2COR3 [R2 = e.g., Ph, PhCH:CH, H, 4-F3CC6H4; R3 = H, Me, Ph; R2R3 = (CH2)5] to give adducts MOCR2R3CRR1NC (I), which are in equil. with 2-metalated oxazolines II. Addn. of MeOH to the reaction mixt. gave oxazolines III, which are

readily hydrolyzed to give .beta.-amine alcs. III are preferably lithiated with BuLi in the 2 position. Depending on the electrophile, trapping experiments gave derivs. of either I or II.

IT **1197-58-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(prepn. and reaction with butyllithium and benzaldehyde)

L10 ANSWER 29 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1976:90078 HCAPLUS
DOCUMENT NUMBER: 84:90078
TITLE: Chemistry of sulfonylmethyl isocyanides. 11. Synthesis of 1,2,4-triazoles from tosylmethyl isocyanide and aryldiazonium compounds
AUTHOR(S): Van Leusen, A. M.; Hoogenboom, B. E.; Houwing, H. A.
CORPORATE SOURCE: Dep. Org. Chem., Univ. Groningen, Groningen, Neth.
SOURCE: Journal of Organic Chemistry (1976), 41(4), 711-13
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
GI For diagram(s), see printed CA Issue.
AB Base-promoted cycloaddn. of p-MeC6H4SO2CH2NC to RN2+X- (R = p-Me2NC6H4, p-MeOC6H4, Ph, p-MeCOC6H4, 3-pyridyl, .alpha.-naphthyl; X = Cl, BF4-) yields the 1,2,4-triazoles I and II. Under the same conditions, the diazonium group is displaced from p-O2NC6H4N2+BF4-.
IT **39495-97-1**
RL: PROC (Process)
(cycloaddn. of, with aryldiazonium salts, triazoles from)

L10 ANSWER 30 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1975:593586 HCAPLUS
DOCUMENT NUMBER: 83:193586
TITLE: Steroidal analogs of unnatural configuration. X. Synthesis of 9-methyl-19-nor-9.beta.,10.alpha.-progesterone
AUTHOR(S): Bull, J. R.; Floor, J.; Tuinman, A.
CORPORATE SOURCE: Natl. Chem. Res. Lab., S. Afr. Counc. Sci. Ind. Res., Pretoria, S. Afr.
SOURCE: Tetrahedron (1975), 31(17), 2157-62
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
GI For diagram(s), see printed CA Issue.
AB The secosteroid I, on successive acetalization, oxidn., reaction with p-MeC6H4SO2CH2NC, and methylation gave a mixt. of the ketone II and its C-20 epimer. Acid hydrolysis of II gave the title compd. (III) and the 5.beta.-hydroxy-3,20-diketone which was converted to III on dehydration. 9-Methyl-19-nor-9.beta.-pregn-5(10)-ene-3,20-dione (IV) was prepd. similarly from 3,3-ethylenedioxy-9-methyl-9.beta.-estr-5(10)-en-17-one.
IT **39495-97-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with estrone deriv.)

L10 ANSWER 31 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1974:424624 HCAPLUS
DOCUMENT NUMBER: 81:24624
TITLE: Isocyanides from alkyl halides and onium dicyanoargentates. Scope and mechanism
AUTHOR(S): Engemyr, Lars B.; Martinsen, Arve; Songstad, Jon
CORPORATE SOURCE: Chem. Inst., Univ. Bergen, Bergen, Norway
SOURCE: Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry (1974), 28(3), 255-66
CODEN: ACAPCT; ISSN: 0302-4377

DOCUMENT TYPE: Journal
LANGUAGE: English
AB Alkyl halides and tetramethylammonium dicyano-argentate gave exclusively the corresponding alkyl isocyanide in .apprx. quant. yield. The reactivity sequence of the alkyl halides was dependent on the alkyl group: tertiary > secondary > primary, and the displaced halide ion: I-> Br-> Cl-. Acyl halides and activated arom. iodides were unreactive toward the dicyanoargentate ion. From a kinetic study in acetonitrile employing some substituted benzhydryl halides, the reactions have been found to be second order, first order in each reactant. The Br-Cl ratio of the rates was dependent on the substrate, being 100 for 4,4'-dimethylbenzhydryl halides but >105 for unsubstituted benzhydryl halides.
IT **52898-02-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

L10 ANSWER 32 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1973:419070 HCAPLUS
DOCUMENT NUMBER: 79:19070
TITLE: Synthesis of amino acids and related compounds. 4. New synthesis of .alpha.-amino acids
AUTHOR(S): Matsumoto, Kazuo; Suzuki, Mamoru; Miyoshi, Muneji
CORPORATE SOURCE: Res. Lab. Appl. Biochem., Tanabe Seiyaku Co. Ltd., Osaka, Japan
SOURCE: Journal of Organic Chemistry (1973), 38(11), 2094-6
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A new synthesis of .alpha.-amino acids by .alpha.-carboxylation of isocyanides is reported. Isocyanides reacted with carboxylating agents in the presence of base to give the corresponding .alpha.-isocyanoacetate derivs., which were hydrolyzed to the amino acids.
IT **1197-58-6 39495-97-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with diethyl carbonate)

L10 ANSWER 33 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1967:37675 HCAPLUS
DOCUMENT NUMBER: 66:37675
TITLE: Aralkyl isonitrile pesticides
INVENTOR(S): Fetzer, Uwe; Eholzer, Ulrich; Ugi, Ivar; Hammann, Ingeborg; Unterstenhoefer, Guenther
SOURCE: Fr., 8 pp.
CODEN: FRXXAK
DOCUMENT TYPE: Patent
LANGUAGE: French
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1441065		19660603		

PRIORITY APPLN. INFO.: DE 19640709
AB Isonitriles R'XAR"N:C useful as insecticides, acaricides, or fungicides, are prepd. from formamides R'XAR"NHCHO by reaction with acyl halides in the presence of a base. Thus, 211 g. N-formylbenzhydrylamine, 2.5 kg. CH2Cl2 (I), and 250 g. NEt3 stirred at 0.degree. is treated with 99 g. COCl2, heated to 15.degree. until no more CO2 evolves and then boiled 15 min. to give 145 g. benzhydrylisonitrile, m. 35-6.degree.. Similarly, N-formyl-4,4'-dichlorobenzhydrylamine gives 4,4'-dichlorobenzhydrylisonitrile, m. 73-4.degree., the corresponding 2,5,4'-trichloro deriv., m. 63-4.degree., and the 4,4'-dimethoxy deriv., m. 124-8.degree.. 1-Formylamino-1,2-diphenylethane, (m. 170.degree., from

benzoin by the Leuckart reaction), (112 g.) in 1 kg. I with 120 g. NEt3 is treated at boiling with 50 g. COCl2, stirred 10 min., excess COCl2 removed by passage of N, NH3 passed to satn., the NH4Cl filtered, the soln. concd., and the residue treated with petroleum ether, to give 32 g. 1-isocyano-1,2-diphenylethane, m. 29-30.degree.. 4-tert-Butylthiophenol and .omega.-chloroacetophenone give 79% 2-phenacyl-4-tert-butylthiophenol, b0.06 180-2.degree., which via the Leuckart reaction gives 93% 1-phenyl-1-formylamino-2-(4-tert-butylphenylmercapto)ethane (II). II, 160 g. in 1 kg. I with 120 g. NEt3 treated over 1 hr. at 5-10.degree. with 50 g. COCl2, warmed, and finally boiled 5 min., then NH3 introduced, the ppt. filtered and the residue evapd., gives 130 g. crude 1-phenyl-2-(tert-butylphenylthio)ethyl-1-isonitrile. These compds. are made up into the usual formulations for pesticidal use. Tests are described against Plutella maculipennis, Myzus persicae, Doralis fabae, and Tetranychus telarius in which 100% kill was obtained using concns. of 0.02-0.2%.

IT **3128-92-5P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

L10 ANSWER 34 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1966:103924 HCAPLUS
DOCUMENT NUMBER: 64:103924
ORIGINAL REFERENCE NO.: 64:19507b-d
TITLE: Insecticidal, acaricidal, and fungicidal isocyanides
PATENT ASSIGNEE(S): Farbenfabriken Bayer A.-G.
SOURCE: 16 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 65008905		19660110	NL	
PRIORITY APPLN. INFO.:			DE	19640709

AB According to the method of the preceding patents, the following isocyanides were prepd.: p-(hexachloronorbornenyl)phenyl isocyanide, m. 167-9.degree.; 3-(.beta.-isocyanoethyl)bicyclo[3.2.2]-3-azanonane, b0.1 104-6.degree.; (norbornenyl)methyl isocyanide, b0.008 36-40.degree.; (hexachloronorbornenyl)methyl isocyanide; 2-isocyanotricyclo[2.2.1.03,5]heptane, b0.1 56.degree.; 3,3-dimethyl-2-[.beta.-isocyano-.beta.-(.omicron.-chlorophenyl)ethylidene]norbornane; 1,2,3,4,7,7-hexachloronorbornenedicarboxylic acid 4-isocyanophenylimide, decompd. at 260.degree.; 2-isocyanotricyclo[2.2.1.03,5]heptane, b0.1 56.degree.; and 3-isocyanotricyclo[5.2.1.02,6]dec-8-ene, b0.002 73-5.degree.. The above isocyanides have low toxicity for warm-blood animals and low phytotoxicity, and are active against Myzus persicae, Aspidiotus hederae, Hercinothrips femoralis, Piesma quadratum, Doralis fabae, Plutella maculipennis, Sitophilus granarius, Agriotes, Blatella germanica, Gryleus domesticus, Reticulitermes, Drosophila melanogaster, Musca domestica, Aedes aegypti, Tetranychus telarius, Eriophyes ribis, Tarsonemus pallidus, Erysiphe, Podosphaera, and Fusarium.

IT **3128-92-5**, Methyl isocyanide, bis(p-methoxyphenyl)-
(prepn. of)

L10 ANSWER 35 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1966:3875 HCAPLUS
DOCUMENT NUMBER: 64:3875
ORIGINAL REFERENCE NO.: 64:643e-h,644a-e
TITLE: Copper isocyanide complexes and preparation thereof
INVENTOR(S): Allison, John A. C.
PATENT ASSIGNEE(S): E. I. du Pont de Nemours & Co.
SOURCE: 5 pp.

DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3197493		19650727	US	19620817

GI For diagram(s), see printed CA Issue.

AB A new class of organometallic compds. having the general structure (RNC)n(CuX)a, where R is an aralkyl group; X is a halo or cyano group; the value of n is 1-5; a is 1 or 2; and n/a is 1-4 are prepd. by the reaction of a simple or complex cupro-cyanide with an alkylating agent, preferably, but not necessarily, in the presence of a diluent. The new compds. are useful for the prepn. of isocyanides, intensely odorous compds., which have been used as additives for gas used in homes and industry for the purpose of detecting and locating leaks. Isocyanides are prepd. from the complexes by treating with an excess of aq. cyanide. Quantitative recoveries are obtained when at least 4 moles of CN- per g. atom of Cu in the complex are employed. When dihalides are employed in the alkylation process, polynuclear isocyanide complexes, containing diisocyanides joined to Cu as Cu-CN-R-NC-Cu linkages, are obtained as products. Diisocyanides are generated from these complexes by treating with aq. cyanide, which are useful as cross-linking agents for polymers containing free OH or NH groups. The compd. (C6H5CH2NC)4CuBr (I) gives complete control of tomato early blight when applied to tomato plants in 0.20% concn. The compd. (C6H5CH2NC)4(CuBr)2 shows a significant change in electrical resistivity with change in temp. making it useful for thermistors. Thus, a mixt. of 85 parts of benzyl bromide, 42.3 parts of KAg2Cu(CN)4, and 330 parts of chlorobenzene is refluxed in a N atmosphere for 4 hrs. The red soln. is filtered while hot from the yellow residue. On standing overnight, white crystals separate from the filtrate. On drying, these crystals amount to 29.5 parts of a compd. ((C6H5CH2NC)3CuAgBr2), 68.3 parts of which are suspended in 275 parts chlorobenzene, heated to the boiling point, filtered from the AgBr liberated and allowed to cool. Again, white crystals separate from the filtrate. After drying, these amount to 38.5 parts of a compd. (C6H5CH2NC)4CuAgBr2. This compd. (16 parts) is put in 320 parts MeOH, raised to the boiling point, filtered hot from the additional AgBr liberated. The filtrate is evaporated under vacuum. The remaining solid is recrystallized from C6H6 to give 12 parts of a white solid, melting at 131.5-133.degree., which is I. The compd. KAg2Cu(CN)4 is prepd. by treating a cold soln. of 285 parts of K3Cu(CN)4 in 600 parts of H2O with 340 parts of AgNO3 in 500 parts of H2O, dropwise and with vigorous stirring over a 2-hr. period. The brown ppt. is stirred for 1 hr. The mixt. is filtered, and the fine powder is washed successively with H2O, EtOH, and (Et)2O, is drained and is dried at 40.degree./100 mm. The product (390 parts) is obtained in 92% conversion. I can also be made by suspending 48 parts of benzyl bromide and 11.4 parts K3Cu(CN)4 in 200 parts CH3CN, refluxing the suspension for 20 hrs., filtering while hot, evaporating the CH3CN, diluting the residual oil with 350 parts of petroleum ether, stirring, filtering off the solid and recrystallizing it from C6H6. The solid, I, is converted to (C6H5CH2NC)4CuCNS by adding a soln. of 6.1 parts of it in 50 parts of aq. MeOH to 1.94 parts of KCNS in 50 parts of H2O. The white ppt. is filtered off, washed with H2O, MeOH and (Et)2O and finally dried. It is recrystallized from C6H6 to give a white solid melting at 140-142.degree.. I is converted to (C6H5CH2NC)4CuClO4 by the above procedure substituting 2.77 parts KClO4 for the KCNS. It melts at 170.degree.. Similar results are also obtained when NaBF4 or AgHSO4 are substituted for the KCNS with the corresponding anion being formed. When I is treated in MeOH with a concd. soln. of iodine in MeOH (C6H5CH2NC)4CuI3 is obtained, melting at 94.5.degree. and having a golden brown color. If this compd. is treated with aq. Na2S2O3 until the color is discharged (C6H5CH2NC)4CuI is obtained as white

crystals melting at 146-147.5.degree.. Other new compds. which have been prepared include: (C6H5CH2NC)3CuBr; II, light brown solid melting at 199.degree.; (2-C10H7CH2NC)2CuCN, colorless flakes melting at 180-181.degree.; III, melting at 159-160.degree.; [(C6H5)3CNC]CuBr, light greenish-brown powder melting at 148.5-150.degree. with decompm.; [(C6H5CH2NC)2CuBr]2; (C6H5CH2NC)3(CuBr)2, melting at 73.5-75.degree.; IV, colorless plates melting at 199-200.degree.; (p-CH3C6H4CH2NC)4CuBr, colorless plates melting at 138-139.degree.; (2,4-Cl2C6H3CH2NC)3CuBr, a white powder melting at 194-195.degree.; (2,4-Cl2C6H3CH2-NC)2CuCN, fluffy white powder melting at 159-160.degree.; [(C6H5)2CHNC]2CuBr,(m-CH3C6H4CH2NC)2CuBr, (p-CH3C6H4CH2NC)2CuBr, (C6H5CH2NC)2CuCl, (2,4-(CH3)3C6H3CH2NC)4CuBr, (3,5-(CH3)2(C6H3CH2NC)4CuI, and V.

IT **4973-73-3**, Methyl isocyanide, p-phenylenebis- **15740-90-6**, Copper, bromotetrakis(p-methylbenzyl isocyanide)- (prepn. of)

L10 ANSWER 36 OF 37 HCAPLUS COPYRIGHT 2003 ACS

ACCESSION NUMBER: 1965:454363 HCAPLUS
DOCUMENT NUMBER: 63:54363
ORIGINAL REFERENCE NO.: 63:9859a-h,9860a-h,9861a
TITLE: Isontrile syntheses
AUTHOR(S): Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offerman, K.
CORPORATE SOURCE: Farbenfabriken Bayer A.-G., Leverkusen, Germany
SOURCE: Angew. Chem. (1965), 77(11), 492-504
DOCUMENT TYPE: Journal
LANGUAGE: German

AB The various methods for prepn. of the title compds. are reviewed and the application of one method is described in detail, viz., dehydration of N-monosubstituted formamides by COCl2 in the presence of teritary amines. Thus, a mixt. of 730 g. HCONHEt, 51.Bu3N, and 31.1,2,4-Cl3C6H3 was prepd., treated during 3-4 hrs. at 20-30.degree. with 1 kg. COCl2, left 1 hr., treated with 100 g. NH3, and distd. to give 65% EtNC, b120 32-5.degree.. The following compds. were prepd. similarly [% yield and b.p. and (or) m.p. are given]: MeNC, 37, b150 25-30.degree.; CH2: CH-CH2NC, 62,-; isoPrNC, 75, b.82-3.degree.; tert-BuNC, 82, b. 92-3.degree.. A soln. of 105g. ClCl2 in 900 ml. CH2Cl2 was added dropwise to a refluxing soln. of 131 g. HCONHCH2CO2Et in 320 ml. Et3N and 500 ml. CH2Cl2. The mixt. was evapd. to dryness in vacuo, treated with 200 ml. C6H5, and filtered. The filtrate was evpd. and the residue distd.to give 77% CNCH2-CO2Et, b4 76-8.degree.. The following compds. were prepd. similarly [% yield, b.p. and (or) m.p. are given]: m-(NC)2C5H4, 74 m. 106-7.degree.; tricyclo[2.2.1.02.6]-2-heptyl isontrile, 84, b1 56-8.degree.; N-methyl-O-(.beta.-isocyanoethyl)urethan, 73, m. 38-9.degree.; 2-furylmethyl isonitrile, 77, b0.02 35-7.degree.; (CH2)4(NC)2, 58, b0.01 70-5.degree.; CN(CH2)2CO2Et, 64, b0.01 39-40.degree.; Cl5C6NC, 64, m. 188-91.degree.; 2,4,6-Br3C6H2NC, 86, m. 113-15.degree.; 3,4-Cl2C6H3NC, 42, m. 32-3.degree.; m-O2NC6H4NC, 93, m. 97-9.degree.; p-O2NC6H4NC, 76, b11 50-1.degree.; Me2CHCH(NC)CO2Me, 76, b15 37-8.degree.; CNCH2Co2Bu-tert, 77, b0.1 38-40.degree.; 2-pyrrolidimoethyl isonitrile, 64, b0.02 46-8.degree.; N-methyl-O-(2-methyl-2-isocyano-2-isocyano-1-propyl)urethan, 73, m. 63-5.degree.; 2-CF3-4-ClC6H3NC, 80, -; 2,4,6-Cl3C6H2CH2NC, 49, m. 134-6.degree.; 2-MeO-3,5,6-Cl3C6HNC, 65,m. 92-3.degree.; o-C6H4(NC)2,32,-;2-MeO-4-No2-5ClC6H2NC,65, m. 117-18.degree.; 2,6-Cl2-C6H3CH2NC, 49, m. 34-5.degree.; 3,4-Cl2C6H3NC,49,m.34-5.degree.; 3,4-Cl2C6H3NC, 46, b0.01 129-30.degree.; 2-MeO-4,5-Cl2C6H2NC, 50, m. 95-6.degree.; p-ClC6H4CH2NC, 54, b0.9 105-10.degree.; 2-Me-3-ClC6H3NC, 79, b0.15 67-8.degree.; 3-Me-4-ClC6H3NC, 48, m. 46-7.degree., b0.006 58-60.degree.; 2-MeO-4-ClC6H3NC, 73, m. 95-7.degree.; 2-MeO-5-ClC6H3NC, 23, m.75-6.degree.; p-O2NC6H4CH2NC, 84, m. 103-4.degree.; 2-Me-5-O2NC6H3NC, 54m. 78-80.degree.; 2-Me-6-O2NC6H3NC, 16 m. 81-6.degree.; 3-O2N-4-MeC6H3NC, 59, m. 75-7.degree.; 2-MeO-4-O2NC6H3NC, 65 m. 158-60.degree.; 2-O2N-4MeOC6H3NC, 60 m. 97-8.degree.;

2-MeO-5-O2NC6H3NC, 87 m. 103-5.degree.; PhCH2NC, 77, b11 92-3.degree.; o-MeC5H4NC, 83, b0.6 36-8.degree.; 1,4-cyclohexanediisonitrile, 43, m. 108-9.degree., b0.1 110-15.degree.; 1-cyanocyclohexyl isonitrile, 73, m. 36-8.degree.; 2-(pentachlorophenylthio)ethyl isonitrile, 97, m. 113-14.degree.; 2,4-(CN)2-C6H3Me, 34, m. 88-9.degree.; 2,6-(CN)2C6H3Me, 32, m. 84-6.degree.; 2,5(CN)2C6H3Me, 72, m. 154-5.degree.; 2-MeO2C-5-O2NC6H3NC, 20, m. 68-70.degree.; 2-MeO-4-Cl-5-MeC6H2NC, 59 m. 93-4.degree.; 2,4-(MeO)2-5-ClC6H2NC, 40, m. 109-10.degree.; 2,4-Me2-5-O2NC6H2NC, 29, m. 50-2.degree.; 2-MeO-4-O2NC6H2NC, 86, m. 134-7.degree.; MeCHPhNC, 87, b0.001 50-4.degree.; 2,5-Me2C6H3NC, 85, b0.01 56-8.degree.; p-MeOC6H4CH2NC, 25, b0.05 90-5.degree.; 2-Me-4-MeOC6H3NC, 27, b0.0001 68-9.degree.; 2,4-(MeO)2C6H3NC,41 m. 67-8.degree.; 2,5-(MeO)2C6H3NC, 65, m. 64-5.degree.; PhS(CH2)2NC 80, b0.001 85-90.degree.; 1,2,3,6-tetrahydro-3,6-methanobenzyl isonitrile, 63, b0.008 36-40.degree.; 1,2,3,6-tetrahydro-5-methylbenzyl isonitrile, 38, b0.04 56-8.degree.; CH2:CMeCO2CH2C(NC)Me2, 37, b0.02 88-92.degree.; Me3CCH2CHMeCH2NC, 56, b3 45-50.degree.; diethyl(2-methyl-2-isocyanopropyl) thionophosphate, 22, b0.004 70-5.degree.; 1,3-(CN)2-4,6-Me2C6H2, 73, m. 105-7.degree.; p-EtO2CC6H4NC, 68, m. 95-103.degree.; 2,4,5-Me3-6-O2NC6HNC, 57, m. 120-6.degree.; PhCMe2NC, 45, b0.003 62-4.degree.; 2,3,5-Me3C6H2NC, 79, b0.4 77-9.degree.; 2,4,5-Me3C6H2ENC, 61, m. 29-31.degree., b0.05 77-80.degree.; 2-MeO-5EtSO2C6H3NC, 74, m. 108-9.degree.; iso-PrCH(NC)CONHCH2CO2Et,79, -; Et2N(CH2)3CHMeNC, 50, b0.1 58-60.degree.; 2,4-dichloro-1-naphthyl isonitrile,79. m. 95-8.degree.; 4-bromo-1-naphthyl isonitrile, 61, m. 88-118.degree. (decompn.); 5,6,7,8-tetrahydro-1-naphthyl isonitrile, 93, b0.02 119-23.degree.; 2,5-(EtO)2-4-O2NC6NC, 57 m. 140.degree. (decompn.); PhCMe2CH2NC, 58, b0.05 68-75.degree.; CO(OCH2CMe2NC)2, 19, m. 114-15.degree.; b0.001 120-5.degree.; 1-(.beta.-isocyanoethyl)-3,6-ethano-hexahydroazepine, 74, b0.1 104-6.degree.; N-(3,4-dicholorophenyl)-O-(2-methyl-2-isocyanopropyl)urethan, 87,m. 122-5.degree.; 1,3-(CNCH2)2-4,6-Me2C6H2,15 m. 68-9.degree.; 1,3(CN)2-2-Me-5-iso-PrC6H2, 24 m. 70-5.degree.; 4-CN-2,6-Et2C6H2Me, 58, b0.002 72-4.degree.; 2-isocyano-2',4,4',5,5'-pentachlorodiphenyl ether, 84 m. 63-4.degree.; 2-phenyl-5-isocyanobenzotriazole, 77 m. 157-9.degree.; 2-isocyanobiphenyl, 70 m. 116-18.degree.; CNC6H4N:NC6H5-p,73, m. 102-4.degree.; 1,3-(CN)2-2,4-Et2-5-Cl-6-MeC5, 54, b0.1 110-15.degree.; 1,3-(CN)2-2,4-Et2-6-MeC6H, 51 b0.5 108-10.degree.; 4-cyclohexylphenyl isonitrile, 91, b0.005 93-5.degree.; 2,4-(iso-Pr)2-5-O2NC6H2NC, 72 m. 70-1.degree.; p-MeC6H4CH(NC)CH2CHMe2, 68, b0.02 98-100.degree.; 2,4-(iso-Pr)2C6H3NC, 82, b0.02 71-2.degree.; 2,6-(iso-Pr)2C6H3NC, 80, b0.7 94-6.degree.; 2,4',5-trichlorobenzhydryl isonitrile, 23, m. 63-4.degree.; (o-CNC6H4)2, 70, 101-4.degree.; p-CNC6H4Bz, 86, m. 79-84.degree.' 4-isocyano-3-methoxybenzofuran, 68,m. 172-3.degree.; Ph2CHNC, 78, m. 35-6.degree.; 3-CN-4-MeOC6H3SO2Ph, 45, m. 115-16.degree.; 1-isocyanoanthraquinone, 31, m. 170.degree. (decompn.); 2-(4-isocyanophenyl)-3,4-benzothiophene 1,1-dioxide, 60,m. 162-3.degree.; PhCH2CHPhNC, 62, m. 29-30.degree.; p-PhC6H4CHMeNC, 47, m. 45-6.degree.; 1,4,5,6,7,7-hexachloro-5-bicyclo[2.2.1]heptene-endo-dicarboxylic acid N-(p-isocyanophenyl)imide, 76, m. >260.degree. (decompn.); 7-isocyano-3-phenylcoumarin, 41, m. 100.degree. (decompn.); (p-MeOC6H4)2CHNC, 88, m. 127-8.degree.; (3-Cl-4-CN-5-MeC6H2)2CH2, 37, m. 208.degree. (decompn.); (3-Me-4-CNC6H3)2CH2, 42, m. 87-9.degree.; 2-(4-isocyano-3-toly)-5,7-dimethylbenzothiazole, 64 m. 129-30.degree.; 1,3-(CN)2-2,4,6-(iso-Pr)3C5H, 69, m. 59-61.degree.; b0.2 130-5.degree.; 4-(.beta.-isocyanoethyl)-2,6-di-tert-butylphenol, 70, m. 114.degree. (decompn.); (3-EtO-4-CNC6H3)2, 65, m. 140-2.degree.; (3-Et-4-CNC6H3)2CH2, 80,m. 83-4.degree.; Me(CH2)17NC 95, -; tris(4-isocyanophenyl) thionophosphate, 13, m. 120-2.degree.; (3-iso-Pr-4-CNC6H3)2CH2, 45, m. 102-26.degree.; [CN-4-MeC6H3O2CNH(CH2)3]2, 42, m. 115-19.degree.; COCl2 (300 g.) was added to a boiling soln. of 178 g. HCONH(CH2)2OH and 1.1 Et3N in 1.5 l. CH2Cl2. The mixt. was treated at 20.degree. with 110 g. NH3 and filtered. The filtrate was evapd to give 86% CO(OCH2CH2NC)2, m. 58-60.degree.. The following compds. were prepd. similarly [% yield and

b.p. and (or) m.p. given]:(CH2NC)2, 64, b0.005 65-8.degree.; BuN, 75, b11 40-2.degree.; 2,6-Br2C6-H3NC, 93, m. 208-9.degree.; 2,6-Cl2C6H3NC, 97,m. 98-100.degree.; cyclohexyl isonitrile, 98, b13 67-72.degree.; 1,3-(CN)2Cl4C, 61, m. 63-5.degree.; 1,4-(CN)2Cl4C6, 84, m. 188-9.degree. (decompn.); p-(CN)2C6H4, 90, m. 100.degree. (decompn.); p-CNC6H4CN, 82,m. 130.degree. (decompn.); p-MeSO2C6H4NC, 85, m. 90-3.degree.; 1,2,3,6-tetrahydrobenzyl isonitrile, 87, b0.01 48-50.degree.; [CN(CH2)3]2, 79, b0.003 92-4.degree.; Et2N-(CN2)3NC, 65, b0.004 40-2.degree.; 2,4-(CN)2-2,5,6-Cl3C6Me, 67, m. 112-16.degree.; m-AcC6H4NC, 97, m. 45-9.degree.; 2,5-(MeO)2-4-ClC6H2NC, 84, m. 150-1.degree.; p-FC6H4CHMeNC, 73, b0.02 59-60.degree.; 2-Cl-4-(Me2NSO2)C6H3NC, 44, m. 98-101.degree.; 2,3-Me2C6H3NC, 82, b0.01 62-3.degree.; 2,4-Me2C6H3NC, 97, b0.03 55-8.degree.; 2,6-Me2C6H3NC, 84, m. 72-3.degree., b0.03 70-5.degree.; [CN(CH2)3]2NMe, 54, b0.2 131-4.degree.; 1,5-(CNCh2)2-2,3,4,5-Cl4C6, 70, m. 170.degree. (decompn.); 8-isocyanoquinoline, 61, m. 69-70.degree.; p-Me2NC6H4CH2NC, 81, m. 40-1.degree.; CN(CH2)2CHMe(CH2)3NC, 76, b0.003 110-15.degree.; .degree.-C10H7NC, 82, b0.005 90-5.degree.; .beta.-C10H7NC, 90, b1 100-2.degree.; 6-isocyano-3-methylquinoline, 93,m. 114-15.degree.; p-MeC6H4CHEtNC, 53, b0.001 70-3.degree.; 2,6-Et2C6H3NC,93, b0.4 70-2.degree.; 2,4-Me2-6-EtC6H2NC, 78, b0.002 72-4.degree.; 1,4-diisocyanonaphthalene, 51; m. 110-12.degree.; 1,5-diisocyanonaphthalene,61, m. 150.degree. (decompn.), 2,7-diisocyanonaphthalene, 93, m. 142-4.degree.; 5-cyano-1-naphthylisonotrile, 69 m. 150.degree. (decompn.); [CN(Ch2)3]3N, 70, -; 2-PhO-3,5-Cl2C6H2NC, 68,m. 120.degree. (decompn.); 3-isocyanobenzofuran, 29, m. 113-14.degree.; 4-isocyanobenzofuran,50, 114-16.degree.; o-CNC6H4SPh, 70, m. 70.degree. (decompn.); o-CNC6H4SO2Ph, 68, m. 78-80.degree.; 2-ethoxy-1-naphthyl isontrile, 89, m. 60-2.degree.; Me(CH2)11NC, 59, b0.01 115-18.degree.; 1,3-(CN)2-4-(Cl5C6S)C6H3, 95, m. 160.degree. (decompn.); (4-CN-2,5-Cl2C6H2)2N2, 65, m. 116.degree. (decompn.); (4-CN-2,6-2Cl2C6H2)2N2, 7, m. 154.degree. (decompn.); (4-CN-3-ClC6H3)2, 88, m. 300.degree. (decompn.); (3-CN-6-ClC6H3-N:)2, 51, m. 152.degree. (decompn.); 2,4-diisocyano-2',4'-dicholorodiphenyl ether, 79, m. 102.degree. (decompn.); (4-CN-3ClC6H3N:)2, 67, m. 132.degree. (decompn.); 2-endo-(p-isocyanophenyl)-1,4,5,-6,7,7-hexachloro-5-bicyclo[2.2.1]heptene, 75, m. 167-8.degree.; 2,4-diisocyano-4'-chlorodiphenyl ether, 67, m. 110.degree. (decompn.); o-CNC6H4C5H4NC-p, 60, m. 97-8.degree.; (p-CNC6H4)2, 94, m. 183-6.degree.; m. 136-7.degree.; (m-CNC6H4N:)2, 71, m. 96-100.degree.; (p-CNC6H4)2-SO2, 93,m. >300.degree. (decompn.); (p-ClC6H4)2CHNC, 72, m. 73-4.degree.; 2-isocyanofluorene, 97, m. 58-9.degree.; o-CNC6H4OC6H4Me-o, 55, m. 37-40.degree., b0.05 113-15.degree.; o-CNC6H4SC5H4Me-o, 83, m. 68-71.degree.; CN(CH2)2CHNC, 87, -; 2,4-(CN)2C6H3C6H4NC-p,83, m. 100.degree. (decompn.); 2,4-(CN)2C6H3OC6H4NC-p, 84,m. 110.degree. (decompn.); [3-Cl-4CNC6H3]2CH2, 20, m. 116-18.degree.; (p-CNC6H4)2CO, 72, m. 120.degree. (decompn.); CO(OC6H4NC-p)2, 76, m. 107-28.degree.; (p-CNC6H4)2CH2, 83, m. 131-3.degree.; 2-(4-isocyanophenyl)-6-methylbenzothiophene, 59, m. 175-6.degree.; 2,5-Cl2C6II3SCII2CHPhNC, 84, -; 3,4-Cl2C6H3SCH2CHPhNC, 98,-; p-ClC6H4CH(NC)CH2Ph, 3, m. 68-9.degree.; p-ClC6H4SCH2CHPhNC, 93, -; 4-CN-3-MeC6H3N:NC6H4Me-o, 80, m. 115-18.degree.; PhSCH2CHPhNC, 83,-; 2-MeO-5-PhCH2SO2C6H3NC, 71, m. 156-7.degree.; [2,4-(CN)2C6H3]2, 68, m. >120.degree. (decompn.); 1,5-diisocyanoanthraquinone, 42, m. 90-2.degree.;(3-Me-4CNC6H3)2, 55, m. 147-9.degree.; [3-MeO-4-(CN)C6H3]2, 93,m. 240-3.degree.; (3-CN-4-MeC6H3Ni]2, 51, m. >130.degree. (decompn.); p-CNC6H4CONEtPh, 58, m. 72-4.degree.; o-MeC6H4SCH2CHPhNC, 88, -; m-MeC6H4SCH2CHPhNC, 96, -; p-MeC6H4SCH2CHPhNC, 91, -; p-(.beta.-C10H7O)C6H4NC, 89, m. 78-80.degree.; p-(.degree.-C10H7S)C6H4NC, 77, m. 113-14.degree.; (3-CN-4-MeOC6H3O)2CO, 87,m. 128-30.degree.; 2,6-Et2-4-CNC6H2N:NC6H4NO2-p, 86,m. 133-6.degree.; (3,5-Me2-4-CNC6H2)2, 68, m. 185-6.degree.; (3,5-Me2-4-CNC6H2)2CH2,72 m. 190.degree. (decompn.); p-Me(CH2)10COC5H4NC, 85, m. 37-43.degree.; [CN(CH2)3]2N(BuCH2PhCl, 84, -; p-Me(CH2)11C6H4NC, 55, m. 39-55.degree.; p-Me(CH2)11OC6H4NC, 72, m. 29-34.degree.; (3-Me-4-CN-5-EtC6H2)2S, 66, m. 81-2.degree.;

m-CNC6H4CONH(CH2)11Me, 54, m. 62-76.degree. (decompn.); [CN(CH2)3]2N(CH2)11Me, 71, -; 4-(p-ClC5H4)C6H4CH(NC)CH2-C6H4Cl-p, 89, m. 116-18.degree.; 3,4-Cl2C6H3SCH2CH(NC)C6H4Ph-p, 92, 74-5.degree.; PhCH2CH(NC)C6H4Ph-p, 31, m. 102-3.degree.; (3-Me-4-CN-5-EtC6H2)CH2, 90, m. 128-30.degree.; Me(CH2)11SCH2CHPh-NC, 84, -; 1,1-bis(3-methyl-4-isocyanophenyl)cyclohexane, 80, m. 142.degree. (decompn.); (4-CN-3,5-Et2C2H2)2S, 72, m. 69-71.degree.; (4-CN-3,5-Et2C6H2)2CH2, 71, m. 98-9.degree.; (4-CN-2,5-Me2C6H2)2-CHPh, 55, m. 102.degree. (decompn.); 2-MeO-5-[Me(CH2)17SO2-NMeC6H3NC, 44, m. 112-20.degree. (decompn.); [CN(CH2)3]2N-[(CH2)17Me]CH2PhCl, 86, -. More than 109 references.

IT **3128-92-5**, Methyl isocyanide, bis(p-methoxyphenyl)-
(prepn. of)

L10 ANSWER 37 OF 37 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1963:64321 HCAPLUS
DOCUMENT NUMBER: 58:64321
ORIGINAL REFERENCE NO.: 58:10960d-f
TITLE: Synthesis and alkylation of [Fe(CN)2(C5H5)(CO)]-, [Mo(CN)2(C5H5)(CO)2]-, [W(CN)2(C2H5)(CO)2]-, and [W(CN)(C5H5)(CO)3]-
AUTHOR(S): Coffey, C. Eugene
CORPORATE SOURCE: E. I. du Pont de Nemours & Co., Wilmington, DE
SOURCE: J. Inorg. Nucl. Chem. (1963), 25, 179-85
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB [Fe(CN)2(C5H5)(CO)]- was best prepd. by reacting [FeBr(C5H5)(CO)2] with KCN in aq. EtOH. Two other syntheses were also found. Alkylation of the anion with alkyl halides gave two series of isocyanide complexes: neutral [Fe(CN)(C5H5)(CO)(CNR)] and cationic [Fe(C5H5)(CO)(CNR)]+. The reaction of KCN with [WCl(C5H5)(CO)3] gave [W(CN)(C5H5)(CO)3] and K[W(CN)2(C5H5)(CO)2]; [MoCl(C5H5)(CO)3] gave only K[Mo(CN)2. (C5H5)(CO)2]. Alkylation of the W monocyanide complex with MeI gave the isocyanide complex [W(C5H5)(CO)3(CNCH3)]I and alkylation of the Mo dicyanide complex gave [Mo(C5H5)(CO)2(CNCH3)2]I. Attempts to form other cyclopentadienylcarbonyl-cyanide complexes were unsuccessful.

IT **97635-67-1**, Iron, cyanocarbonylcyclopentadienyl(.alpha.-isocyano-p-toluic acid)- **99080-18-9**, Iron, cyanocarbonylcyclopentadienyl(.alpha.-isocyano-p-toluic acid)-, ethyl ester
(prepn. of)

=>
=> fil caold
FILE 'CAOLD' ENTERED AT 11:48:28 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

FILE COVERS 1907-1966
FILE LAST UPDATED: 01 May 1997 (19970501/UP)

This file contains CAS Registry Numbers for easy and accurate substance identification. Title keywords, authors, patent assignees, and patent information, e.g., patent numbers, are now searchable from 1907-1966. TIFF images of CA abstracts printed between 1907-1966 are available in the PAGE display formats.

This file supports REG1stRY for direct browsing and searching of all substance data from the REGISTRY file. Enter HELP FIRST for more information.

=>

```
=>

=> s l9
L11         13 L9

=> d all l11 1-9

L11  ANSWER 1 OF 13  CAOLD  COPYRIGHT 2003 ACS
AN   CA64:19507b  CAOLD
TI   isocyanides (insecticidal, acaricidal, and fungicidal)
PA   Farbenfabriken Bayer A.-G.
DT   Patent
     PATENT NO.     KIND          DATE
     ------------   -----------   ----
PI   NL 6508904
     BE 666566
     DE 1215142
     GB 1047007
PI   NL 6508905
     BE 666567
IT   3126-29-2   3126-47-4   3128-81-2   3128-85-6   3128-88-9
     3128-92-5   3805-55-8   5554-08-5   5554-09-6   5554-12-1
     5554-13-2   5554-14-3   7398-41-6

L11  ANSWER 2 OF 13  CAOLD  COPYRIGHT 2003 ACS
AN   CA64:643e  CAOLD
TI   Cu isocyanide complexes and prepn. thereof
AU   Allison, John A. C.
DT   Patent
TI   copper isocyanide complexes and prepn. thereof
PA   Du Pont de Nemours, E. I., & Co.
DT   Patent
     PATENT NO.     KIND          DATE
     ------------   -----------   ----
PI   US 3197493                   1965
IT   4973-73-3  12194-60-4  12203-90-6  12204-29-4  15200-48-3
     15454-18-9  15604-87-2  15632-88-9  15680-17-8  15738-91-7  15738-92-8
     15738-93-9  15738-96-2  15738-97-3  15740-79-1  15740-90-6
     105765-07-9

L11  ANSWER 3 OF 13  CAOLD  COPYRIGHT 2003 ACS
AN   CA63:9859a  CAOLD
TI   isonitrile syntheses
AU   Ugi, Ivar; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K.
IT    950-95-8    951-12-2    952-28-3    958-10-1    958-95-2    962-37-8
     968-14-9    968-15-0    974-08-3   1019-08-5   1034-13-5   1079-98-7
     1124-57-8   1125-42-4   1128-04-7   1195-99-9   1197-36-0
     1197-58-6   1930-79-6   1930-80-9   1930-81-0   1930-82-1
     1930-84-3   1930-86-5   1930-87-6   1930-88-7   1930-89-8   1930-90-1
     1930-92-3   1930-93-4   1930-94-5   1930-95-6   1930-96-7   1930-97-8
     1983-95-5   1983-96-6   1983-97-7   1983-98-8   1983-99-9   1984-00-5
     1984-01-6   1984-02-7   1984-20-9   1984-21-0   1984-22-1   1984-23-2
     2008-60-8   2008-61-9   2008-62-0   2456-94-2   2456-97-5   2769-71-3
     2920-07-2   2920-08-3   2920-09-4   2920-10-7   2920-11-8   2920-12-9
     2920-24-3   2920-29-8   2980-80-5   2980-81-6   2980-82-7   2980-84-9
     2980-85-0   2980-86-1   2980-89-4   2980-90-7   2980-91-8   2980-92-9
     2980-93-0   2980-94-1   2980-95-2   2980-97-4   2980-98-5   2980-99-6
     2981-01-3   2982-60-7   2982-76-5   2999-46-4   2999-47-5   2999-48-6
     2999-49-7   2999-50-0   2999-51-1   2999-52-2   2999-53-3   2999-54-4
     3097-77-6   3097-78-7   3097-79-8   3097-80-1   3097-81-2   3097-82-3
     3097-83-4   3097-84-5   3097-85-6   3097-86-7   3097-87-8   3097-88-9
     3097-89-0   3097-90-3   3097-91-4   3097-92-5   3097-93-6   3097-94-7
     3097-95-8   3097-96-9   3097-97-0   3097-98-1   3097-99-2   3098-00-8
```

3100-70-7	3100-92-3	3100-93-4	3101-17-5	3101-18-6	3101-19-7
3117-74-6	3117-75-7	3117-77-9	3117-78-0	3117-79-1	3117-82-6
3117-83-7	3117-84-8	3117-85-9	3117-86-0	3117-87-1	3117-88-2
3117-89-3	3117-91-7	3117-93-9	3117-95-1	3117-96-2	3117-97-3
3117-98-4	3117-99-5	3126-28-1	3126-29-2	3126-30-5	3126-31-6
3126-32-7	3126-33-8	3126-35-0	3126-37-2	3126-38-3	3126-40-7
3126-41-8	3126-42-9	3126-43-0	3126-45-2	3126-46-3	3126-47-4
3126-48-5	3126-50-9	3126-51-0	3126-52-1	3128-75-4	3128-76-5
3128-77-6	3128-81-2	3128-83-4	3128-84-5	3128-85-6	3128-86-7
3128-87-8	3128-88-9	3128-89-0	3128-90-3	3128-91-4	
3128-92-5	3128-94-7	3128-95-8	3128-97-0	3128-98-1	
3128-99-2	3133-20-8	3133-21-9	3133-22-0	3133-23-1	3136-50-3
3136-51-4	3136-66-1	3138-30-5	3138-31-6	3138-32-7	3138-33-8
3138-34-9	3195-67-3	3218-14-2	3345-51-5	3472-30-8	3805-55-8
4004-06-2	4311-91-5	5178-87-0	5554-09-6	5554-13-2	

L11 ANSWER 4 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA63:4482d CAOLD
TI cross-linking in latexes of polymers of unsatd. carboxylic acids
PA Farbenfabriken Bayer A.-G.
DT Patent
TI plastics casing for fluorescent lamps
AU Fowler, Kenneth E.; Vause, A. S.; Robbins, D.
DT Patent

PATENT NO.	KIND	DATE
GB 992415		
NL 6410022		
BE 652056		
FR 1407388		

IT

78-94-4	106-68-3	141-79-7	544-60-5	929-57-7	2424-61-5
2456-86-2	2456-94-2	**2456-96-4**	2456-97-5	3117-89-3	
3965-08-0					

L11 ANSWER 5 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA62:11744c CAOLD
TI aralkyl isonitriles-agricultural pesticides
AU Fetzer, Uwe; Ugi, I.; Unterstenhoefer, G.; Behrenz, W.; Frohberger, P. E.
PA Farbenfabriken Bayer A.-G.
DT Patent

PATENT NO.	KIND	DATE
FR 1379917		
BE 641311		
DE 1211853		
GB 994616		
NL 301906		

IT

635-51-8	1124-57-8	1125-42-4	1128-04-7	1135-74-6	1156-00-9
1195-99-9	1197-36-0	**1197-58-6**	1808-19-1		

L11 ANSWER 6 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA59:10977g CAOLD
TI reactions of coordinated ligands - (VII) structure and reactivity of Fe(II) benzyl isonitrile complexes
AU Heldt, Walter Z.
IT 15334-29-9 15616-63-4 15616-66-7 **105071-15-6** 106217-71-4 **107873-20-1** 107895-79-4 108037-85-0 108151-56-0 108151-91-3 108167-06-2 108171-71-7 108374-45-4 108755-55-1

L11 ANSWER 7 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA59:10128b CAOLD
TI cyclopentadienylnickel nitrosyl compds.
AU Feltham, Robert D.; Anzenberger, J. F.; Carriel, J. T.

PA International Nickel Co., Inc.
DT Patent

PATENT NO.	KIND	DATE
US 3088959		1963

IT 12071-73-7 32714-42-4 108126-69-8 108171-73-9 **108986-61-4**

L11 ANSWER 8 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA59:10127h CAOLD
TI terpenes - (XIII) structure of sylvestrene
AU Punnoose, Mathew C.; Verghese, J.
IT 17092-82-9 23516-31-6 105045-69-0 108172-12-9 108172-44-7
108271-31-4 108271-32-5 108538-48-3 108565-86-2
108986-37-4 108987-29-7

L11 ANSWER 9 OF 13 CAOLD COPYRIGHT 2003 ACS
AN CA59:10127d CAOLD
TI Fe isonitrile complexes
AU Heldt, Walter Z.
DT Patent
TI iron isonitrile complexes
PA Du Pont de Nemours, E. I., & Co.
DT Patent

PATENT NO.	KIND	DATE
US 3085103		1963

IT **105071-15-6**

=>
=>

=> fil reg
FILE 'REGISTRY' ENTERED AT 11:48:52 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 12 MAR 2003 HIGHEST RN 498527-50-7
DICTIONARY FILE UPDATES: 12 MAR 2003 HIGHEST RN 498527-50-7

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

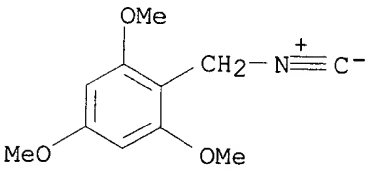
Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=>
=>

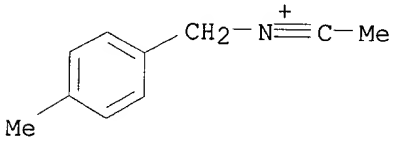
=> d ide can 19 tot

L9 ANSWER 1 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 480438-26-4 REGISTRY

CN Benzene, 2-(isocyanomethyl)-1,3,5-trimethoxy- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C11 H13 N O3
SR CAS Registry Services



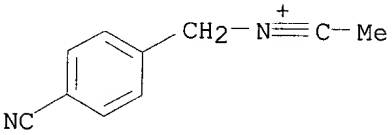
L9 ANSWER 2 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 388596-84-7 REGISTRY
CN Benzenemethanaminium, N-ethylidyne-4-methyl- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C10 H12 N
SR CA
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 136:101996

L9 ANSWER 3 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 388596-68-7 REGISTRY
CN Benzenemethanaminium, 4-cyano-N-ethylidyne- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C10 H9 N2
SR CA
LC STN Files: CA, CAPLUS

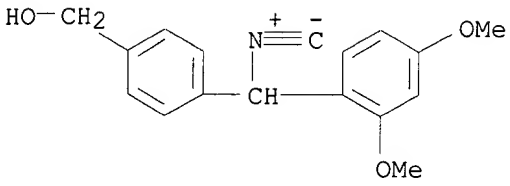


1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 136:101996

L9 ANSWER 4 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 344594-17-8 REGISTRY
CN Benzenemethanol, 4-[(2,4-dimethoxyphenyl)isocyanomethyl]- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C17 H17 N O3

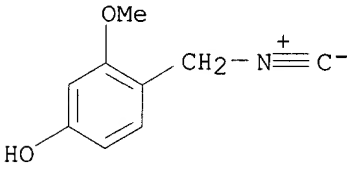
SR CA
LC STN Files: CA, CAPLUS, CASREACT



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 135:46139

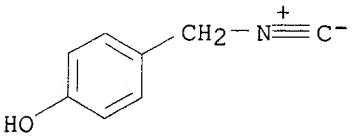
L9 ANSWER 5 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 342773-61-9 REGISTRY
CN Phenol, 4-(isocyanomethyl)-3-methoxy- (9CI) (CA INDEX NAME)
OTHER NAMES:
CN 4-(Isocyanomethyl)-3-methoxyphenol
FS 3D CONCORD
MF C9 H9 N O2
SR CA
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 135:19230

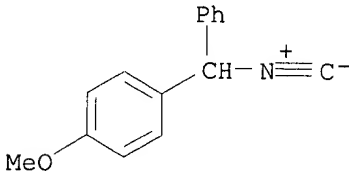
L9 ANSWER 6 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 342773-60-8 REGISTRY
CN Phenol, 4-(isocyanomethyl)- (9CI) (CA INDEX NAME)
OTHER NAMES:
CN 4-(Isocyanomethyl)phenol
FS 3D CONCORD
MF C8 H7 N O
SR CA
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 135:19230

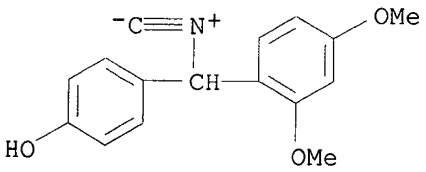
L9 ANSWER 7 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 342773-59-5 REGISTRY
CN Benzene, 1-(isocyanophenylmethyl)-4-methoxy- (9CI) (CA INDEX NAME)
OTHER NAMES:
CN Isocyano(4-methoxyphenyl)phenylmethane
FS 3D CONCORD
MF C15 H13 N O
SR CA
LC STN Files: CA, CAPLUS, CASREACT



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 135:19230

L9 ANSWER 8 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 342395-21-5 REGISTRY
CN Phenol, 4-[(2,4-dimethoxyphenyl)isocyanomethyl]- (9CI) (CA INDEX NAME)
OTHER NAMES:
CN 4-[Isocyano(2,4-dimethoxyphenyl)methyl]phenol
FS 3D CONCORD
MF C16 H15 N O3
SR CA
LC STN Files: CA, CAPLUS, TOXCENTER



3 REFERENCES IN FILE CA (1962 TO DATE)
2 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
3 REFERENCES IN FILE CAPLUS (1962 TO DATE)

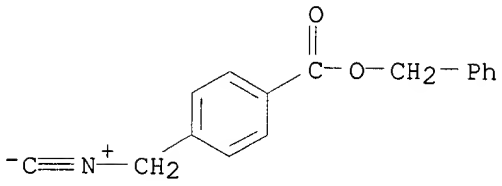
REFERENCE 1: 137:279443

REFERENCE 2: 135:46203

REFERENCE 3: 135:19230

L9 ANSWER 9 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 244221-06-5 REGISTRY
CN Benzoic acid, 4-(isocyanomethyl)-, phenylmethyl ester (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C16 H13 N O2

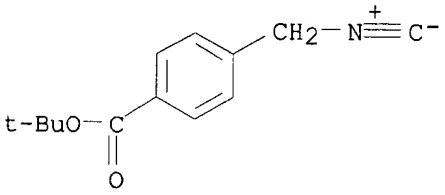
SR CA
LC STN Files: CA, CAPLUS, USPATFULL



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 131:243287

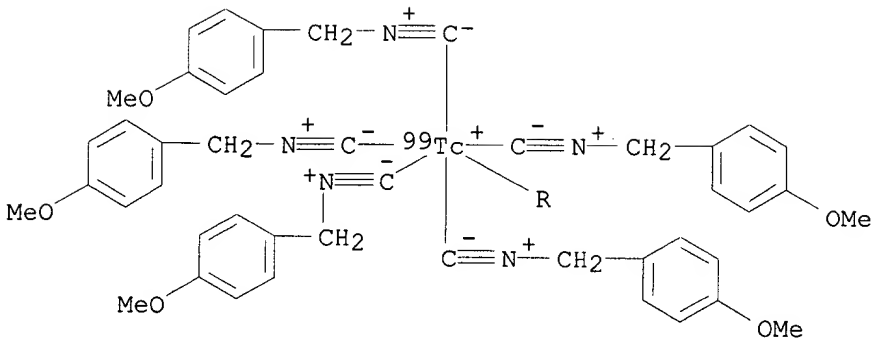
L9 ANSWER 10 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 244221-05-4 REGISTRY
CN Benzoic acid, 4-(isocyanomethyl)-, 1,1-dimethylethyl ester (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C13 H15 N O2
SR CA
LC STN Files: CA, CAPLUS, USPATFULL

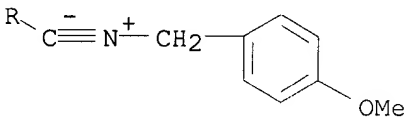


1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 131:243287

L9 ANSWER 11 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 165459-89-2 REGISTRY
CN Technetium(1+)-99Tc, hexakis[1-(isocyanomethyl)-4-methoxybenzene]-, (OC-6-11)- (9CI) (CA INDEX NAME)
MF C54 H54 N6 O6 Tc
CI CCS
SR CA
LC STN Files: CA, CAPLUS

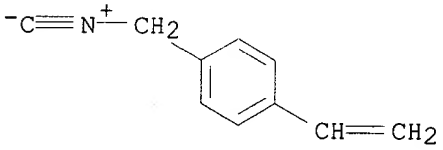




1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 123:78638

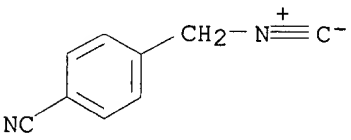
L9 ANSWER 12 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 160654-51-3 REGISTRY
CN Benzene, 1-ethenyl-4-(isocyanomethyl)- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C10 H9 N
SR CA
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 122:105352

L9 ANSWER 13 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 130287-23-9 REGISTRY
CN Benzonitrile, 4-(isocyanomethyl)- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C9 H6 N2
SR CA
LC STN Files: CA, CAPLUS

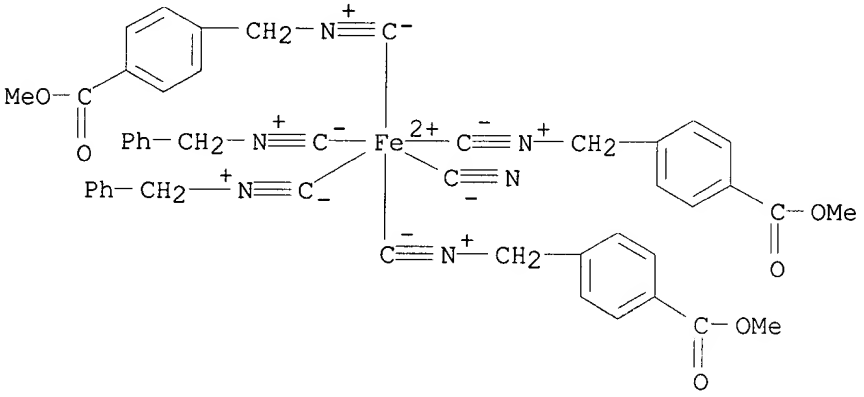


2 REFERENCES IN FILE CA (1962 TO DATE)
2 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 125:32963

REFERENCE 2: 113:211059

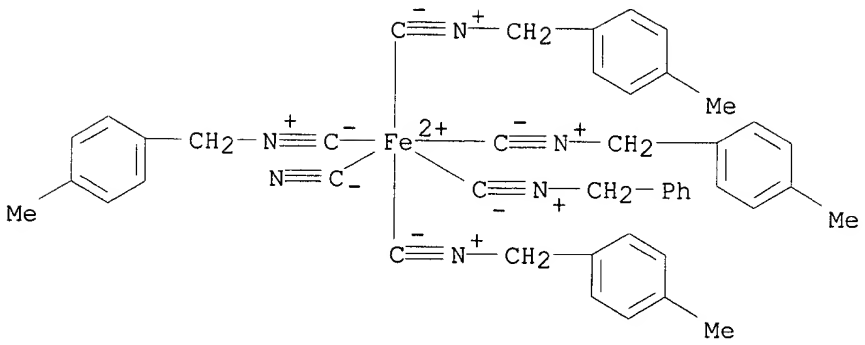
L9 ANSWER 14 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108987-29-7 REGISTRY
CN Cyanobis(benzyl isocyanide)tri(.alpha.-isocyano-p-toluic acid)iron bromide, trimethyl ester (7CI) (CA INDEX NAME)
MF C47 H41 Fe N6 O6 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD



● Br^-

2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 15 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108986-61-4 REGISTRY
CN Cyano(benzyl isocyanide)tetrakis(p-methylbenzyl isocyanide)iron bromide (7CI) (CA INDEX NAME)
MF C45 H43 Fe N6 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD

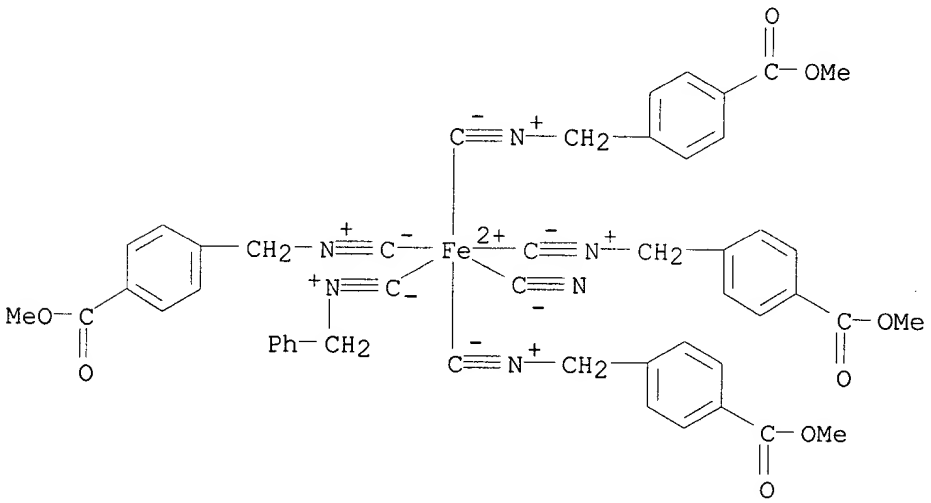


● Br^-

2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 16 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108986-37-4 REGISTRY
CN Cyano(benzyl isocyanide)tetrakis(.alpha.-isocyano-p-toluic acid)iron bromide, tetramethyl ester (7CI) (CA INDEX NAME)
MF C49 H43 Fe N6 O8 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD

PAGE 1-A



PAGE 2-A

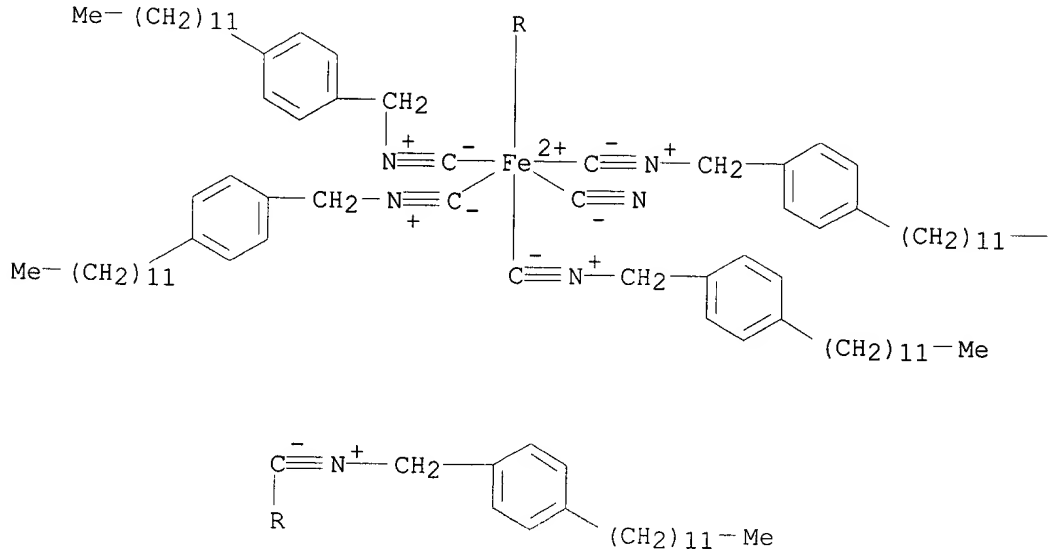
● Br^-

2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 17 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108271-32-5 REGISTRY

CN Cyanopentakis(p-dodecylbenzyl isocyanide)iron chloride (7CI) (CA INDEX NAME)
MF C101 H155 Fe N6 . Cl
CI CCS
SR CAOLD
LC STN Files: CAOLD

PAGE 1-A



PAGE 1-B

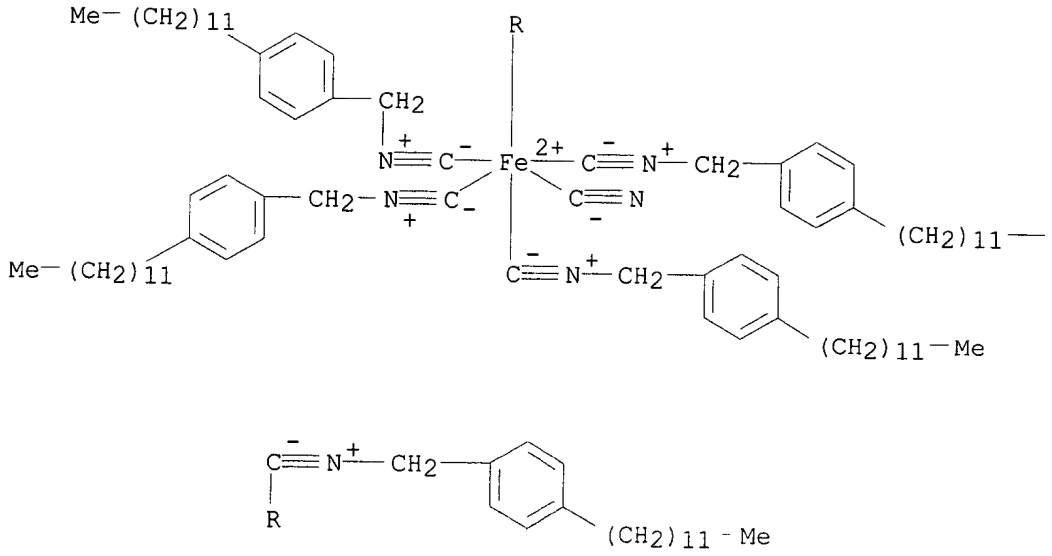
— Me

● Cl^-

1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 18 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108271-31-4 REGISTRY
CN Cyanopentakis(p-dodecylbenzyl isocyanide)iron bromide (7CI) (CA INDEX NAME)
MF C101 H155 Fe N6 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD

PAGE 1-A



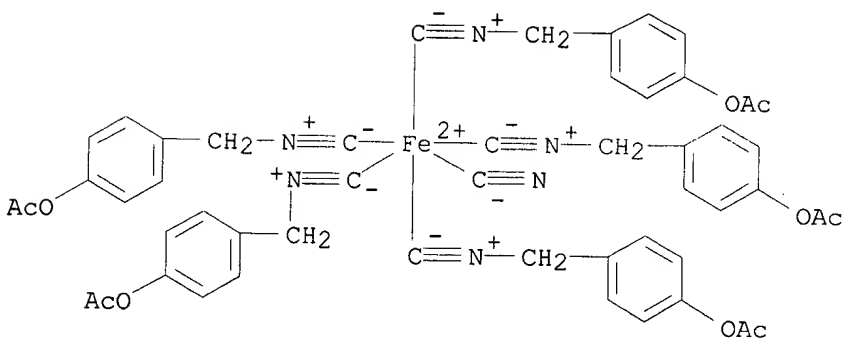
PAGE 1-B

— Me

● Br^-

1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

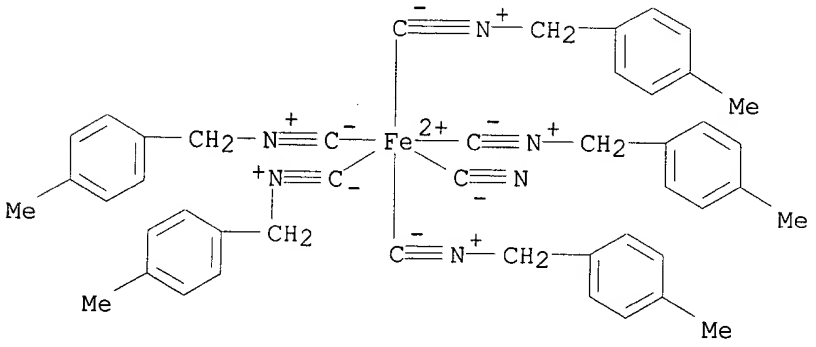
L9 ANSWER 19 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 108270-64-0 REGISTRY
CN Cyanopentakis(p-hydroxybenzyl isocyanide)iron bromide, acetate (7CI) (CA INDEX NAME)
MF C51 H45 Fe N6 O10 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD



● Br^-

1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 20 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 107873-20-1 REGISTRY
CN Cyanopentakis(p-methylbenzyl isocyanide)iron bromide (7CI) (CA INDEX NAME)
MF C46 H45 Fe N6 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD

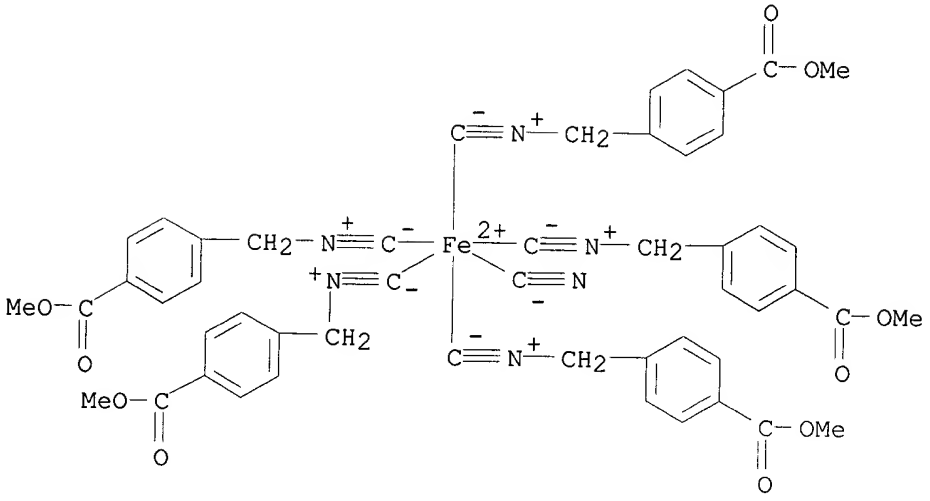


● Br^-

4 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 21 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 105071-15-6 REGISTRY
CN Cyanopentakis(.alpha.-isocyano-p-toluic acid)iron bromide, pentamethyl ester (7CI) (CA INDEX NAME)
MF C51 H45 Fe N6 O10 . Br
CI CCS
SR CAOLD
LC STN Files: CAOLD

PAGE 1-A

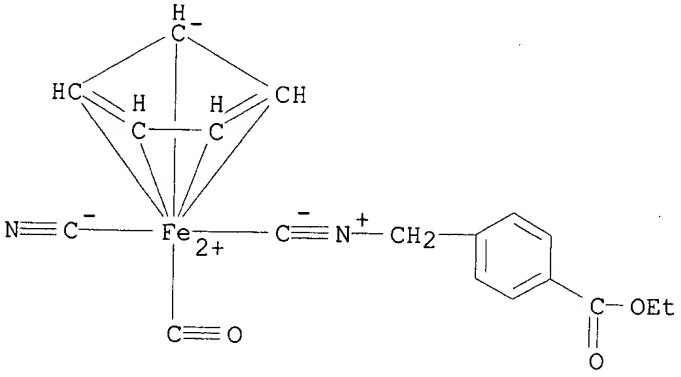


PAGE 2-A

● Br^-

4 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 22 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 99080-18-9 REGISTRY
CN Iron, cyanocarbonylcyclopentadienyl(.alpha.-isocyano-p-toluic acid)-, ethyl ester (7CI) (CA INDEX NAME)
MF C18 H16 Fe N2 O3
CI CCS
SR CAOLD
LC STN Files: CA, CAOLD, CAPLUS

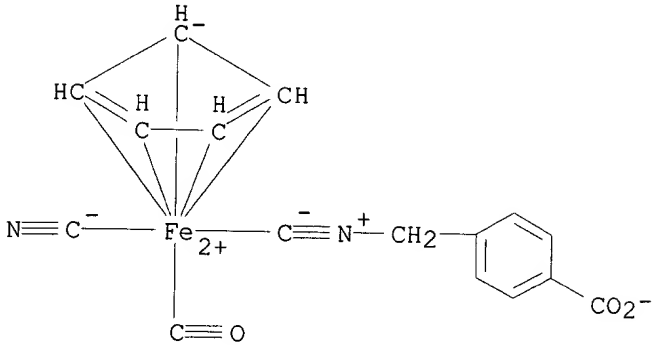


1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 58:64321

L9 ANSWER 23 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 97635-67-1 REGISTRY
CN Iron, cyanocarbonylcyclopentadienyl(.alpha.-isocyano-p-toluic acid)- (7CI)

(CA INDEX NAME)
MF C16 H11 Fe N2 O3 . H
CI CCS
SR CAOLD
LC STN Files: CA, CAOLD, CAPLUS



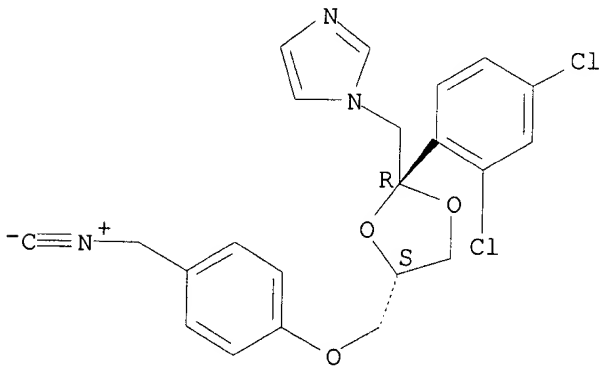
● H^+

1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 58:64321

L9 ANSWER 24 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 82966-03-8 REGISTRY
CN 1H-Imidazole, 1-[[2-(2,4-dichlorophenyl)-4-[[4-(isocyanomethyl)phenoxy]methyl]-1,3-dioxolan-2-yl]methyl]-, cis- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C22 H19 Cl2 N3 O3
LC STN Files: CA, CAPLUS, TOXCENTER, USPATFULL

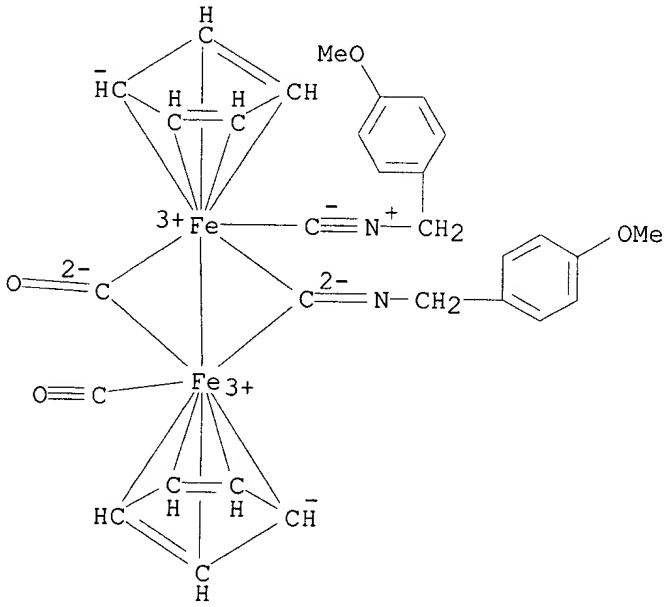
Relative stereochemistry.



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 97:127638

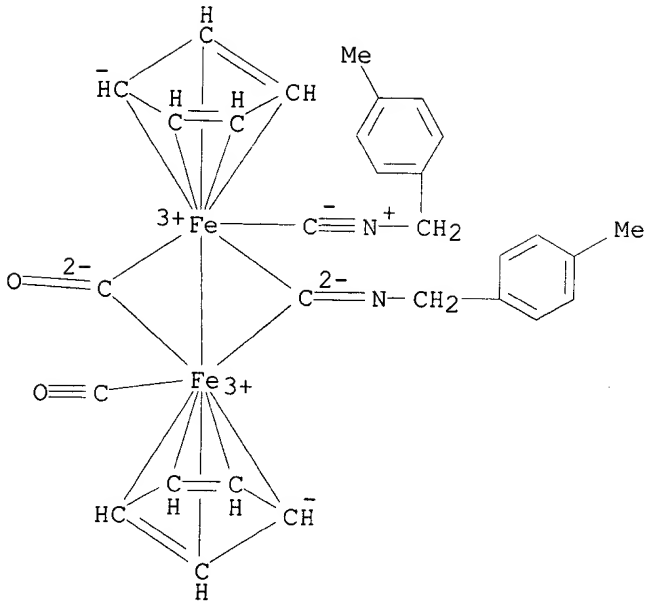
L9 ANSWER 25 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 78656-49-2 REGISTRY
CN Iron, .mu.-carbonylcarbonylbis(.eta.5-2,4-cyclopentadien-1-yl)[1-(isocyanomethyl)-4-methoxybenzene][.mu.-[[(4-methoxyphenyl)methyl]carbonimidoyl]]di-, (Fe-Fe), stereoisomer (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methoxy-, iron complex
CN Benzenemethanamine, 4-methoxy-N-methylene-, iron complex
MF C30 H28 Fe2 N2 O4
CI CCS
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 95:96698

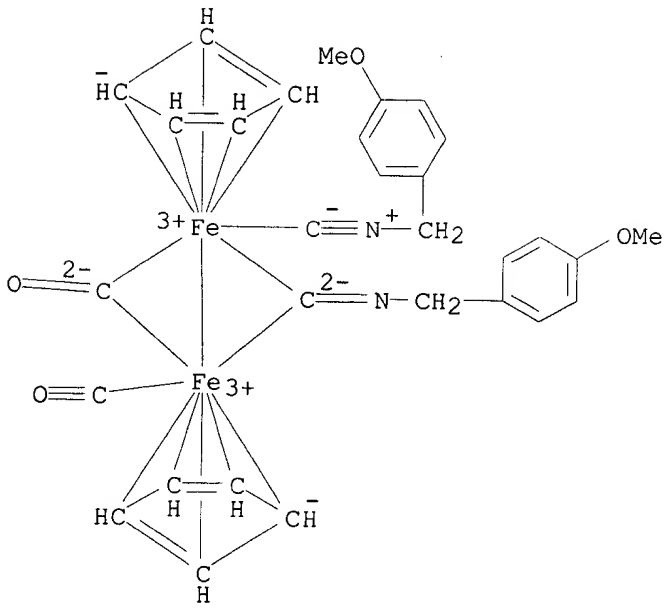
L9 ANSWER 26 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 78656-47-0 REGISTRY
CN Iron, .mu.-carbonylcarbonylbis(.eta.5-2,4-cyclopentadien-1-yl)[1-(isocyanomethyl)-4-methylbenzene][.mu.-[[(4-methylphenyl)methyl]carbonimidoyl]]di-, (Fe-Fe), stereoisomer (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methyl-, iron complex
CN Benzenemethanamine, 4-methyl-N-methylene-, iron complex
MF C30 H28 Fe2 N2 O2
CI CCS
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 95:96698

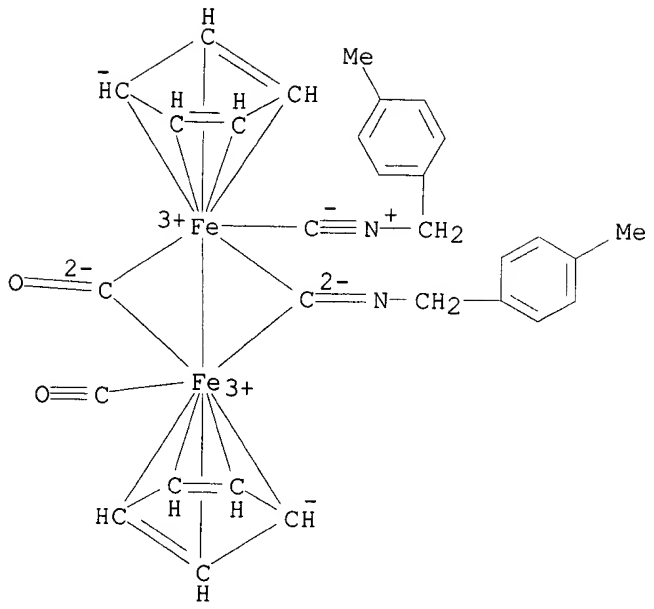
L9 ANSWER 27 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 78618-61-8 REGISTRY
CN Iron, .mu.-carbonylcarbonylbis(.eta.5-2,4-cyclopentadien-1-yl)[1-(isocyanomethyl)-4-methoxybenzene][.mu.-[[(4-methoxyphenyl)methyl]carbonimidoyl]]di-, (Fe-Fe), stereoisomer (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methoxy-, iron complex
CN Benzenemethanamine, 4-methoxy-N-methylene-, iron complex
MF C30 H28 Fe2 N2 O4
CI CCS
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 95:96698

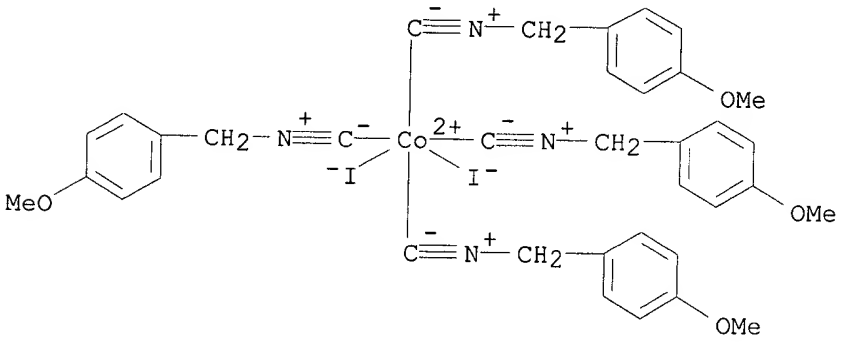
L9 ANSWER 28 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 78618-59-4 REGISTRY
CN Iron, .mu.-carbonylcarbonylbis(.eta.5-2,4-cyclopentadien-1-yl)[1-(isocyanomethyl)-4-methylbenzene][.mu.-[[(4-methylphenyl)methyl]carbonimidoyl]]di-, (Fe-Fe), stereoisomer (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methyl-, iron complex
CN Benzenemethanamine, 4-methyl-N-methylene-, iron complex
MF C30 H28 Fe2 N2 O2
CI CCS
LC STN Files: CA, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 95:96698

L9 ANSWER 29 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 61770-66-9 REGISTRY
CN Cobalt, diiodotetrakis[1-(isocyanomethyl)-4-methoxybenzene]-, (OC-6-12)-(9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methoxy-, cobalt complex
MF C36 H36 Co I2 N4 O4
CI CCS
LC STN Files: CA, CAPLUS

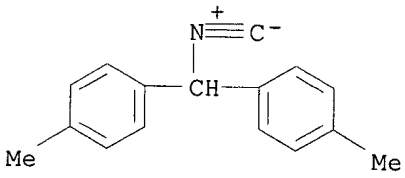


1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 86:54792

L9 ANSWER 30 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 52898-02-9 REGISTRY
CN Benzene, 1,1'-(isocyanomethylene)bis[4-methyl- (9CI) (CA INDEX NAME)

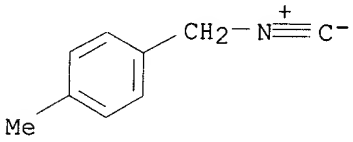
FS 3D CONCORD
MF C16 H15 N
LC STN Files: BEILSTEIN*, CA, CAPLUS
(*File contains numerically searchable property data)



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 81:24624

L9 ANSWER 31 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 39495-97-1 REGISTRY
CN Benzene, 1-(isocyanomethyl)-4-methyl- (9CI) (CA INDEX NAME)
FS 3D CONCORD
MF C9 H9 N
LC STN Files: BEILSTEIN*, CA, CAPLUS, CHEMCATS, GMELIN*
(*File contains numerically searchable property data)



4 REFERENCES IN FILE CA (1962 TO DATE)
4 REFERENCES IN FILE CAPLUS (1962 TO DATE)

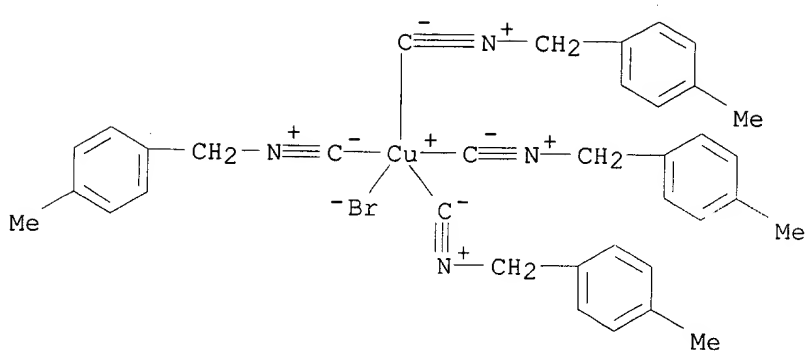
REFERENCE 1: 113:211059

REFERENCE 2: 84:90078

REFERENCE 3: 83:193586

REFERENCE 4: 79:19070

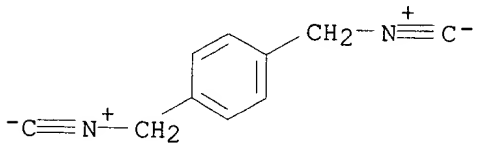
L9 ANSWER 32 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 15740-90-6 REGISTRY
CN Copper, bromotetrakis[1-(isocyanomethyl)-4-methylbenzene]- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzene, 1-(isocyanomethyl)-4-methyl-, copper complex
CN Copper, bromotetrakis(p-methylbenzyl isocyanide)- (7CI)
MF C36 H36 Br Cu N4
CI CCS
LC STN Files: CA, CAOLD, CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 64:3875

L9 ANSWER 33 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 4973-73-3 REGISTRY
CN Benzene, 1,4-bis(isocyanomethyl)- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Methyl isocyanide, p-phenylenebis- (7CI, 8CI)
FS 3D CONCORD
MF C10 H8 N2
LC STN Files: CA, CAOLD, CAPLUS

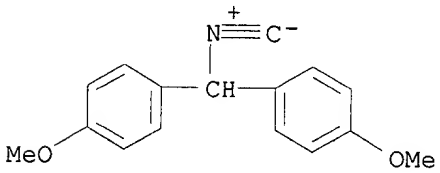


2 REFERENCES IN FILE CA (1962 TO DATE)
2 REFERENCES IN FILE CAPLUS (1962 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 129:45739

REFERENCE 2: 64:3875

L9 ANSWER 34 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 3128-92-5 REGISTRY
CN Methyl isocyanide, bis(p-methoxyphenyl)- (7CI, 8CI) (CA INDEX NAME)
FS 3D CONCORD
MF C16 H15 N O2
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, TOXCENTER
(*File contains numerically searchable property data)



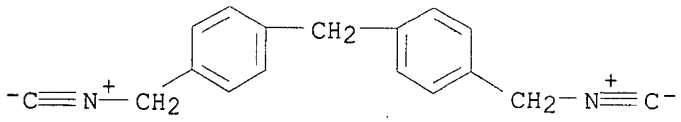
3 REFERENCES IN FILE CA (1962 TO DATE)
3 REFERENCES IN FILE CAPLUS (1962 TO DATE)
2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 66:37675

REFERENCE 2: 64:103924

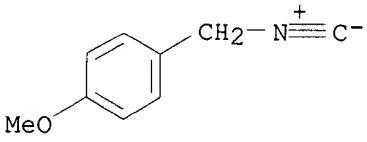
REFERENCE 3: 63:54363

L9 ANSWER 35 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 2456-96-4 REGISTRY
CN Benzyl isocyanide, 4,4'-methylenebis- (7CI, 8CI) (CA INDEX NAME)
FS 3D CONCORD
MF C17 H14 N2
LC STN Files: CAOLD



1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L9 ANSWER 36 OF 36 REGISTRY COPYRIGHT 2003 ACS
RN 1197-58-6 REGISTRY
CN Benzene, 1-(isocyanomethyl)-4-methoxy- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzyl isocyanide, p-methoxy- (7CI, 8CI)
OTHER NAMES:
CN 4-Methoxybenzyl isocyanide
FS 3D CONCORD
MF C9 H9 N O
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, USPATFULL
(*File contains numerically searchable property data)



17 REFERENCES IN FILE CA (1962 TO DATE)
17 REFERENCES IN FILE CAPLUS (1962 TO DATE)
2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 132:63776

REFERENCE 2: 131:115835

REFERENCE 3: 131:87685

REFERENCE 4: 131:44656

REFERENCE 5: 128:140349

REFERENCE 6: 127:293136

REFERENCE 7: 126:18629

REFERENCE 8: 125:195502

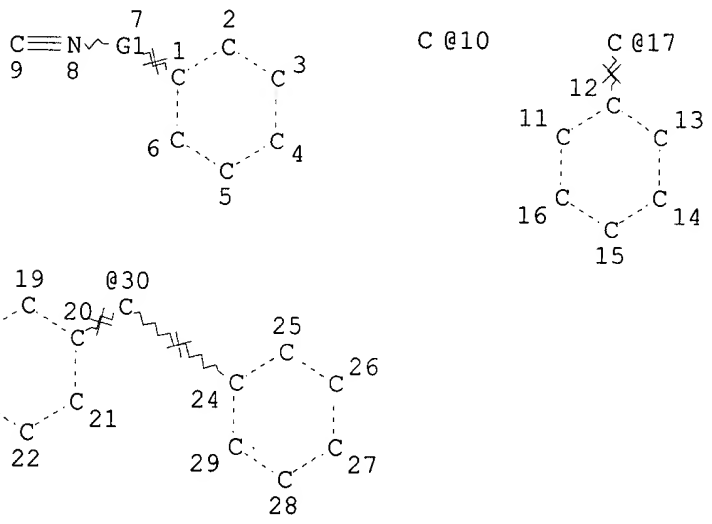
REFERENCE 9: 125:157765

REFERENCE 10: 123:78638

```
=> fil hcaplus
FILE 'HCAPLUS' ENTERED AT 11:51:53 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)
```

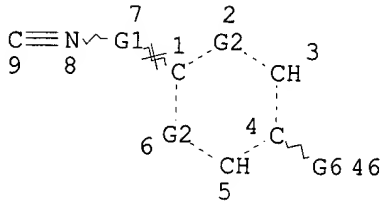


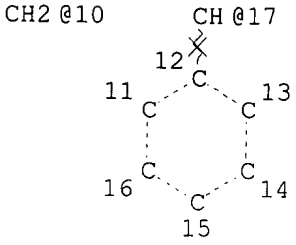
```
FILE COVERS 1907 - 13 Mar 2003  VOL 138 ISS 11
FILE LAST UPDATED: 12 Mar 2003  (20030312/ED)

 This file contains CAS Registry Numbers for easy and accurate
 substance identification.

=>
=>

=> d stat que
L1                  STR
```

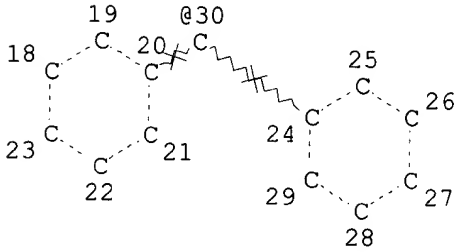


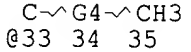

```
VAR G1=10/17/30
NODE ATTRIBUTES:
NSPEC   IS RC     AT  10
NSPEC   IS RC     AT  17
NSPEC   IS RC     AT  30
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS  30

STEREO ATTRIBUTES: NONE
```

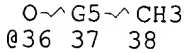
L5 1338 SEA FILE=REGISTRY SSS FUL L1
L8 STR





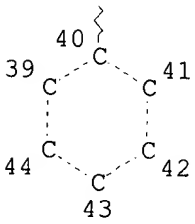






O @45

Page 1-A



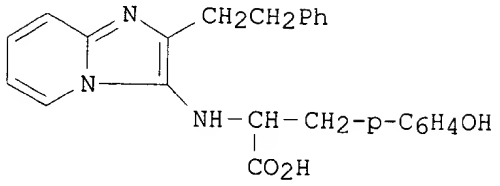
Page 2-A
VAR G1=10/17/30
VAR G2=CH/31
VAR G3=ME/ET/I-PR/N-PR/I-BU/N-BU/T-BU/S-BU/33/36/45
REP G4=(3-4) C
REP G5=(0-5) C
VAR G6=O/C
NODE ATTRIBUTES:
NSPEC IS RC AT 30
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 46

STEREO ATTRIBUTES: NONE
L9 36 SEA FILE=REGISTRY SUB=L5 SSS FUL L8
L10 37 SEA FILE=HCAPLUS ABB=ON PLU=ON L9
L12 464 SEA FILE=REGISTRY ABB=ON PLU=ON ISONITR?
L13 17185 SEA FILE=HCAPLUS ABB=ON PLU=ON L12 OR ?ISONITR?

```
L14          306 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)REAGENT
L17         1686 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)(SOLUTION OR SOLID(W)PHA
                 SE)
L18       126770 SEA FILE=HCAPLUS ABB=ON  PLU=ON  SYNTHE?(L)(SOLUTION OR
                 SOLID(W)PHASE)
L19           17 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L14 AND L17 AND L18
L20           16 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L19 NOT L10


=>
=>

=> d ibib abs hitrn l20 1-16

L20  ANSWER 1 OF 16  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:         2002:190776  HCAPLUS
TITLE:                    A facile three-step one-pot synthesis of norstatines
                          using the passerini reaction
AUTHOR(S):                Tadesse, Seifu; Balan, Chenera; Jones, Wyeth;
                          Viswanadhan, Vellarkad; Hulme, Christopher
CORPORATE SOURCE:         Department of Small Molecule Drug Discovery, Amgen,
                          Thousand oaks, CA, 91320, USA
SOURCE:                   Abstracts of Papers, 223rd ACS National Meeting,
                          Orlando, FL, United States, April 7-11, 2002 (2002),
                          ORGN-241.  American Chemical Society: Washington, D.
                          C.
                          CODEN: 69CKQP
DOCUMENT TYPE:            Conference; Meeting Abstract
LANGUAGE:                 English
AB   Combinatorial chem. has been used as a platform for generating chem.
     libraries in both the lead generation and hit-to-lead arenas by most
     pharmaceutical companies.  In fact, recent advances in automation have
     resulted in highly efficient syntheses of a variety of complex
     drug-like mols. via both solid and soln. phase reactions.  In an
     inhouse effort to rapidly build a preferred collection of potential
     aspartyl protease inhibitors, a soln. phase parallel
     synthesis approach, coupled with a solid phase
     scavenging step, was developed to generate norstatines via the Passerini
     reaction.  Such efforts utilized two scavenging steps with resin bound
     scavenging reagents (PS-tosylhydrazine and PS-NMM), producing
     highly diverse and high quality (> 70% as judged by UV220 nM) arrays of
     this biol. relevant transition state isostere.  The prodn. of > 20,000
     norstatines, from readily available N-t-BOC aminoaldehydes, 1,
     isonitriles, 2, and carboxylic acids, 3, was routinely carried out
     according to Scheme 1, utilizing Tom-tech (Quadra '96) and Rapid plate
     96-well dispensers.  As such, the methodol. described herein, represents
     the Passerini version of the previously reported two step
     synthesis of dihydroimidazoles, 6, from reaction of N-t-BOC
     aminoaldehydes in the Ugi, followed by deprotection and cyclization (UDC -
     Ugi/De-BOC/Cyclize), Scheme 2.

L20  ANSWER 2 OF 16  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:         2001:585625  HCAPLUS
DOCUMENT NUMBER:          135:318674
TITLE:                    Multi-component synthesis of imidazo[1,2-a] annulated
                          heterocycles on .alpha.-isocyano resin esters
AUTHOR(S):                Chen, Jack J.; Golebiowski, Adam; Klopfenstein, Sean
                          R.; McClenaghan, Joel; Peng, Sean X.; Portlock, David
                          E.; West, Laura
CORPORATE SOURCE:         Combinatorial Chemistry Group, Procter and Gamble
                          Pharmaceuticals, Mason, OH, 45040, USA
SOURCE:                   Synlett (2001), (8), 1263-1265
                          CODEN: SYNLES; ISSN: 0936-5214
```

PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:318674
GI



I

AB The multi-component **synthesis** of imidazo[1,2-a] annulated heterocycles, e.g. I, was performed on the .alpha.-isocyano resin esters. This **solid phase** approach addresses the limited availability issue of **isonitrile reagents** without compromising the overall diversity of the chem.
REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L20 ANSWER 3 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:498884 HCAPLUS
DOCUMENT NUMBER: 135:331409
TITLE: MCC/SNAr methodology. Part 1: Novel access to a range of heterocyclic cores
AUTHOR(S): Tempest, P.; Ma, V.; Kelly, M. G.; Jones, W.; Hulme, C.
CORPORATE SOURCE: Department of Combinatorial Chemistry, AMGEN Inc., Thousand Oaks, CA, 91320, USA
SOURCE: Tetrahedron Letters (2001), 42(30), 4963-4968
CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The novel **soln.**-phase **syntheses** of arrays of biol. relevant indazolinones, benzazepines and benzoxazepines, utilizing multi-component condensation (MCC)/SNAr methodol. is reported. Reaction of com. available 2-fluoro-5-nitrobenzoic acid with an aldehyde, **isonitrile** and a primary amine tethered to a Boc-protected internal amino or hydroxyl nucleophile, affords the Ugi product in good yield. Subsequent acid treatment followed by proton scavenging using polymer-supported **reagents** promotes cyclization of internal amino nucleophiles to a variety of ring sizes. Base treatment alone is sufficient to generate benzoxazepines. Interestingly, this method also introduces a highly efficient two-step route to benzimidazoles.
IT **598-45-8**, Isopropyl isocyanide **931-53-3**, Cyclohexyl isocyanide **2769-71-3**, 2,6-Dimethylphenyl isocyanide **7188-38-7**, tert.-Butyl isocyanide **10340-91-7**, Benzyl isocyanide
RL: RCT (Reactant); RACT (Reactant or reagent)
(**soln.**-phase prepn. of heterocyclic compds. by multi-component condensation using polymer-supported **reagents**)
REFERENCE COUNT: 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L20 ANSWER 4 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2000:632652 HCAPLUS

DOCUMENT NUMBER: 133:350379
TITLE: **Solution** Phase **Synthesis** of Libraries of Polycyclic Natural Product Analogues by Cascade Radical Annulation: **Synthesis** of a 64-Member Library of Mappicine Analogues and a 48-Member Library of Mappicine Ketone Analogues
AUTHOR(S): de Frutos, Oscar; Curran, Dennis P.
CORPORATE SOURCE: Department of Chemistry and Center for Combinatorial Chemistry, University of Pittsburgh, Pittsburgh, PA, 15260, USA
SOURCE: Journal of Combinatorial Chemistry (2000), 2(6), 639-649
CODEN: JCCHFF; ISSN: 1520-4766
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 133:350379

AB An improved cascade radical annulation route to (.+-.)-mappicine, (S)-mappicine, and mappicine ketone is reported. The route is used to prep. libraries of mappicine and mappicine ketone analogs in a semiautomated fashion. Key diversity generating steps include the addn. of an aldehyde to a Grignard **reagent** derived from a D-ring iodopyridine, N-propargylation of a subsequently derived iodopyridone, and cascade radical annulation with an **isonitrile** to form a mappicine analog. Parallel oxidn. of mappicine analogs produced mappicine ketones. The route is general and flexible and could be used to make very large libraries. It is also illustrative of how late stage cascade reactions can be employed strategically to generate libraries of polycyclic natural product analogs.

IT **931-54-4**, Phenyl **isonitrile** **7175-47-5**, 4-Methylphenyl **isonitrile** **10349-38-9**, 4-Methoxyphenyl **isonitrile** **24075-34-1**, 4-Fluorophenyl **isonitrile**
RL: RCT (Reactant); RACT (Reactant or reagent)
(**soln.** phase **synthesis** of libraries of mappicine and mappicine ketone analogs via cascade radical annulation)

REFERENCE COUNT: 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L20 ANSWER 5 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1986:417294 HCAPLUS
DOCUMENT NUMBER: 105:17294
TITLE: Spectrophotometric study of copper complex of N-benzylisonitrosoacetylacetonimine
AUTHOR(S): Lee, Byung Kyo; O, Dae Sub; Lee, Heung Lark
CORPORATE SOURCE: Dep. Chem., Kyungpook Natl. Univ., Daegu, 635, S. Korea
SOURCE: Taehan Hwahakhoe Chi (1986), 30(2), 201-6
CODEN: DHWHAB; ISSN: 0418-2472
DOCUMENT TYPE: Journal
LANGUAGE: Korean

AB A new anal. **reagent** N-**benzylisonitrosoacetylacetonimine** (H-IAA-N-Bz) was **synthesized** and identified by IR, NMR, and mass spectra. H-IAA-N-Bz forms a Cu CHCl3-sol. complex in a basic aq. **soln.** (pH = 7.0-10.0). The other optimum conditions for the spectrophotometric study of the Cu complex were detd. at 420 nm. Beer's law is obeyed for <64 .mu.g Cu/10 mL CHCl3. The complex is formulated as Cu(IAA-N-Bz)2, with an over-all stability const. of 8.55 .times. 106. The molar absorptivity of Cu-(IAA-N-Bz)2 is 3500 L/cm.mol.

L20 ANSWER 6 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1971:483827 HCAPLUS
DOCUMENT NUMBER: 75:83827
TITLE: **Isonitrosoacetylacetone** as an extractant and

spectrophotometric **reagent** for nickel(II)
AUTHOR(S): Talwar, U. B.; Haldar, B. C.
CORPORATE SOURCE: Inorg. Nucl. Chem. Lab., Inst. Sci., Bombay, India
SOURCE: Indian Journal of Chemistry (1971), 9(6), 593-6
CODEN: IJOCAP; ISSN: 0019-5103
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A method is described for the sepn. and spectrophotometric detn. of Ni in **synthetic** mixts., stainless steel, and Cu-Ni alloy by extn. with **isonitrosoacetylacetone** (HINAA). The av. of 8 detns. with 8.5 .mu.g of Ni in 10 ml **soln.** is 8.48 .mu.g which varies between 8.30 and 8.55 at 95% confidence limit. The sequential sepn. of Ni(II), Fe(I), Co(II), and Pd(II), and simultaneous spectrophotometric detn. of Ni(II), Fe(II), and Pd(II) have been achieved.

L20 ANSWER 7 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1968:31828 HCAPLUS
DOCUMENT NUMBER: 68:31828
TITLE: Removal of metals from lubricating oils and colorimetric analysis for metal content
INVENTOR(S): Doyle, Doris M.
PATENT ASSIGNEE(S): Boeing Co.
SOURCE: Fr., 7 pp.
CODEN: FRXXAK
DOCUMENT TYPE: Patent
LANGUAGE: French
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1460393		19661125		
PRIORITY APPLN. INFO.:			US	19641218

AB Metals, esp. Fe, and their compds., e.g. rust, in suspension or **soln.** in **synthetic** or petroleum lubricating oils, can be removed by washing the oil with an immiscible liq. that dissolves the metal after it has been chem. transformed by the action of **reagents** also added to the oil. In the case of Fe, it is usually necessary to change its valence state before it can be extd. from the oil. The concn. of metal in the ext., and hence that in the oil, can be detd. by transforming it into a colored compd. and comparison with known standards, applying Beer's law. Thus, 6 ml. (5 g.) of oil from a helicopter transmission was placed in a 250-ml. flask with 10 ml. each of Et2O 50% aq. HCl, and 30% aq. H2O2, added in that order. The mixt. was shaken vigorously for .apprx.5 min. The aq. phase was then decanted and filtered to eliminate traces of oil, and 10 ml. each of the HCl and H2O2 **solns.** were again added to the oil and the mixt. shaken, sepd., and filtered as before. Finally the oil phase was shaken with 30 ml. of the H2O2 **soln.** plus 10 ml. distd. H2O for .apprx.3 min. after which 5 ml. 50% HCl was added and the flask again shaken for .apprx.5 min. and the aq. phase sepd. and filtered, followed by 2 washings by using 5 ml. each of H2O. The accumulated aq. phase mixt. was stirred or shaken until homogeneous, and 2 g. solid NH2OH.HCl was added very slowly, the reaction being strongly exothermic and producing a large vol. of gas. Finally, 10 ml. of a 0.1% by wt. **soln.** of 1,10-phenanthroline was added to produce a bright orange color, which was stabilized by adjusting the pH of the mixt. to 4-6 by addn. of .apprx.16 ml. concd. NH4OH. The color of the final mixt. remained stable for 6-12 months. NaO2 or KMnO4 may be used in place of H2O2 and iso-Pr2O, iso-BuCOMe, AmOH, amyl alc., or a CHCl3 **soln.** of **diisonitrosoacetophenone** for Et2O.

L20 ANSWER 8 OF 16 HCAPLUS COPYRIGHT 2003 ACS

ACCESSION NUMBER: 1967:443490 HCAPLUS
DOCUMENT NUMBER: 67:43490
TITLE: Preparation of cardiac- and circulatorty-active compounds
AUTHOR(S): Schulz, Heinz
CORPORATE SOURCE: Pharm. Forschungsabt, VEB Fahlberg-List, Magdeburg, Fed. Rep. Ger.
SOURCE: Pharmazie (1967), 22(1), 19-22
CODEN: PHARAT; ISSN: 0031-7144
DOCUMENT TYPE: Journal
LANGUAGE: German
GI For diagram(s), see printed CA Issue.
AB Substituted aromatic .alpha.-alkylamino ketones were prepd from substituted aromatic aryl alkyl ketones, the latter being prepd. by the Friedel-Crafts **synthesis** from the corresponding acid chloride, substituted benzene, and AlCl3. By halogenation of the ketone at 70.degree. in the presence of alkali carbonate in an inert solvent, good yields of the substituted aromatic .alpha.-alkylamino ketone were obtained by condensing with the appropriate amine in the same inert solvent. The following derivs. (I) of 1-phenyl 2-isopropylaminopropanone-HCl salt were prepd. (R1, R2, R3, R4, R5, and m.p. given): Me, Me, H, Cl, Cl, 210.degree.; Me, Me, H, Me, Cl, 194.degree.; Me, iso-Pr, H, Cl, Cl, 225.degree.; Et, iso-Pr, H, Cl, Cl, 235-8.degree.; Me, CH2CH2OH, CH2CH2OH, Cl, Cl, 173-5.degree.; Me, (R2R3 =) CH2CH2OCH2CH2, Cl, Cl, 217.degree.; Me, CHMeCH2Ph, H, Cl, Cl, 200-3.degree.; Me, iso-Pr, H, H, MeO, 208-10.degree.; Me, iso-Pr, H, H, MeO, 225-7.degree.; Me, (R2R3 =) CH2CH2OCH2CH2, H, MeO, 217-18.degree.; Et, iso-Pr, H, MeO, MeO, 230-2.degree.. I were reduced with Raney Ni or PtO2 in an alc. solvent, usually MeOH, at 40.degree. and pH 8, producing the resp. substituted aromatic .alpha.-alkylamino alc. in good yields. The solvent was distilled off, HCl added to form the salt, and the product crystd. from iso-PrOH or H2O. The following II were reported (R1, R2, R3, R4, R5, and m.p. given): Me, Me, H, Cl, Cl, 234-6.degree.; Me, Me, H, Me, Cl, 224-6.degree.; Me, iso-Pr, H, Cl, Cl, 225.degree.; Et, iso-Pr, H, Cl, Cl, 250-2.degree.; Me, CH2CH2OH, CH2CH2OH, Cl, Cl, 142-6.degree.; Me, (R2R3 =) CH2CH2OCH2CH2, Cl, Cl, 226.degree.; Me, CHMeCH2Ph, H, Cl, Cl, 167.degree.; Me, iso-Pr, H, H, MeO, 186-8.degree.; Me, iso-Pr, H, MeO, MeO, 210.degree.; Me, (R2R3 =) CH2CH2OCH2CH2, H, MeO, 190-1.degree.; Et, iso-Pr, H, MeO, MeO, 208-10.degree.. Other similar alcs. were prepd. from substituted aromatic .alpha.-amino alcs., which in turn were prepd. from aryl alkyl ketones. Thus, 3,6-dichloropropiophenone in C6H6 was treated with HCl gas cooled to 5.degree., MeOH, NaNO2, and H2SO4, which was added until no red color formed, and the mixt. was stirred 30 min. at a temp. below 20.degree. to give 3,4 **dichlorophenylisonitrosopropiophenone**, m. 152.degree.. This was then reduced with Raney Ni to give 1-(3,4-dichlorophenyl)-2-amino-1-propanol, m. 114.degree.; HCl salt m. 192.degree.. A condensation reaction with a Schiff base (prepd. from amino alc. and anisaldehyde) was effected and the product hydrogenated at 40.degree. in the presence of Raney's Ni to form the following .alpha.-alkylamino alcs. (III) (R1, R2, R3, R4, and m.p. given): H, H, Cl, Cl, 193.degree.; p-CH2C6H4OMe, H, H, H, 180-1.degree.; p-CH2C6H4OMe, H, Cl, Cl, 229.degree.; o-CH2C6H4Cl, H, Cl, Cl, 229.degree.; CH2CHMePr, H, Cl, Cl, 171-3.degree.; CH2CH2CHPh2, H, Cl, Cl, 267.degree.. Substituted aromatic .alpha.-alkylaminoisobutyrophenones were prepd. by the following procedure. Br, isobutyrophenone, and soda in C6H6, was refluxed with Na in MeOH, to yield 1-methoxy-1,2-epoxyisobutylbenzene, which was heated 10 hrs. at 200.degree. with MeNH2-satd. benzene, cooled, and HCl added to give 1-phenyl-2-methylaminoisobutyrophenone-HCl (IV), m. 212-14.degree.. The following V were similarly prepd. (R1, R2, R3, and m.p. given): iso-Pr, H, H, 231.degree.; Me, H, Cl, 239-40.degree.; iso-Pr, iso-Pr, H, Cl, 245-7.degree.; iso-Pr, MeO, MeO, 246-8.degree.. In another series, by halogenation of the substituted aromatic .alpha.-alkylamino ketones followed by hydrogenation, the corresponding substituted aromatic

.alpha.-alkylamino alcs. could be obtained. Thus, MeOH **soln.** of IV was treated with Raney Ni at 40.degree. and pH 8 2 hrs. to complete the hydrogenation. Addn. of HCl and recovery of solvent left 1-phenyl-2-methylaminoisobutanol-HCl, m. 228-30.degree.. Others of this series were VI (R1, R2, R3, and m.p. given): iso-Pr, H, H, 228-30.degree.; Me, H, Cl, 208-10.degree.; iso-Pr, H, Cl, 248-50.degree.; iso-Pr, MeO, MeO, 200-2.degree.. By reacting the substituted aromatic .alpha.-amino- or .alpha.-alkylamino alcs. with halogenation **reagents**, such as SOCl2, the OH group is replaced by halide. Halogenation is carried out by suspending the finely divided precursor in C6H6, adding the halogenating agent dropwise at room temp., and heating the mixt. to boiling. The halogen can then be replaced by H in the prepn. of substituted aromatic amines by hydrogenating in the presence of a catalyst, such as Raney Ni and AcONa in alc. solvent. Another way of prepg. substituted aromatic secondary amines is by treating aromatic primary amines with aldehydes and hydrogenating the Schiff bases in the presence of catalysts, such as Raney Ni in alc. solvent base. The following VII were prepd. by one or other of these means (R1, R2, R3, R4, R5, R6, and m.p. given): H, Me, iso-Pr, Cl, Cl, Cl, 190.degree.; H, Me, iso-Pr, H, Cl, Cl, 185-6.degree.; H, Me, CH2CH2CHPh2, H, Cl, Cl, 227.degree.; Me, Me, Me, Cl, H, H, 186-8.degree.; Me, Me, Me, H, H, H, 171-3.degree.; Me, Me, Me, Cl, H, Cl, 212-14.degree.; Me, Me, Me, H, H, Cl, 181-3.degree.; Me, Me, iso-Pr, Cl, H, H, 188-90.degree.; Me, Me, iso-Pr, H, H, H, 176-8.degree.; Me, Me, iso-Pr, Cl, MeO, MeO, 160-2.degree.; Me, Me, iso-Pr, H, MeO, MeO, 150-2.degree.. The compds. prepd. were tested for their activity on the circulation and esp. for their antiarrhythmic activity.

L20 ANSWER 9 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1961:92305 HCAPLUS
DOCUMENT NUMBER: 55:92305
ORIGINAL REFERENCE NO.: 55:17362i,17363a-b
TITLE: Analytical use of 1,3-dimethyl-4-imino-5-hydroxyiminoalloxan. I. Determination of copper
AUTHOR(S): Burger, K.
CORPORATE SOURCE: L. Eotvos Univ., Budapest, Hung.
SOURCE: Talanta (1961), 8, 77-84
DOCUMENT TYPE: Journal
LANGUAGE: English

AB A new red cryst. **reagent** for metals, 1,3-dimethyl-4-imino-5-hydroxyiminoalloxan (I) prepd. by Traube **synthesis**, contains 2 functional groups; an **isonitroso**-imino group selective for Ni++ and Pd++, and an **isonitroso**-keto .dblharw. nitroso-enol, selectively forming H2O-sol. colored complexes with Cu++, Fe++, and Co++. I is insol. in CHCl3, alcs., Et2O, and dioxane, slightly sol. in Me2CO and in H2O, but sol. in HCONH2 and in alkalies. The acid dissocn. const. of I, detd. by potentiometric titration of the alk. **soln.**, is 1 .times. 10-8. Cu++ forms a 1:1 complex with 1% I in HCONH2 with a max. at pH 8 of 382 m.mu.. The molar absorptivity of the Cu-I complex prepd. from 1-13 .gamma. Cu++/ml. is (5.05 .+-. 0.05) .times. 103 at 25.degree.. Recoveries of 1-13 .gamma. Cu++ have an av. error of .+-. 0.8% Hg++, Pb++, Bi+++, Mn++, Zn++, Cd++, Ba++, Fe+++, Al+++, Ca++, Mg++, Na+, or Sb+++ do not interfere in concns. of 4000, 830, 250, 220, 260, 440, 560, 68, 32, 160, 96, 100, and 500 .gamma./ml., resp. Co++, Pd++, Ni++, and Fe++ interfere. The av. error in detg. 7.7 .gamma. Cu in the presence of each of the noninterfering ions is .+-.1.5%.

L20 ANSWER 10 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1959:56451 HCAPLUS
DOCUMENT NUMBER: 53:56451
ORIGINAL REFERENCE NO.: 53:10222a-i,10223a-b
TITLE: Fluorinated isatins and some of their heterocyclic derivatives
AUTHOR(S): Yen, V. Q.; Buu-Hoi, Ng Ph.; Xuong, Ng D.

CORPORATE SOURCE: Univ. Paris
SOURCE: J. Org. Chem. (1958), 23, 1858-61
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB The Sandmeyer isatin **synthesis** was applied with success to 4-fluoro- (I), 3,4-difluoro- (II), and 4-bromo-3-fluoroaniline (III), while 2-fluoro- (IV), and 2,4-difluoroaniline (V) failed to give the corresponding isatins. The fluorinated isatins thus obtained were used for the **synthesis** of a large no. of F contg. quinolines, acridines, and indophenazines required for testing as potential carcinogens. CCl3CH(OH)2 (90 g.) and 1300 g. Na2SO4 in 1200 ml. H2O was refluxed 2 min. with 55.5 g. I and 110 g. NH2OH.HCl in 800 ml. H2O and 43 ml. HCl, cooled, and the p-**fluoroisonitrosoacetanilide** collected and purified (88 g.), m. 160.degree.; a byproduct m. 302.degree. (AcOH). This **isonitroso** compd. (87 g.) added portionwise to 360 ml. H2SO4 at 60-70.degree., then raised to 80.degree. 20 min., cooled, the product poured on crushed ice, and the product collected gave 44 g. 5-fluoroisatin (VI), brick red needles, m. 227.degree. (aq. AcOH); oxime m. 275.degree. (alc.). VI (2.5 g.) and 1.6 g. .omicron.-(H2N)2C6H4 in 10 ml. AcOH refluxed 15 min. gave 2.5 g. 9-fluoroindophenazine (VII), yellow needles, m. 302.degree., orange-red halochromy with H2SO4. VII (0.5 g.) in 10 ml. Ac2O refluxed 15 min. gave 0.4 g. 6-acetyl-9-fluoroindophenazine, m. 201.degree. (AcOH), orange halochromism with H2SO4. VI (5.5 g.) and 7 g. PCl5 in 22 ml. anhyd. C6H6 gave 3.5 g. 5-fluoroisatin enol .alpha.-chloro deriv. (VIII), m. 201.degree. (decompn.) (C6H6). VIII (3 g.) suspended in 40 ml. AcOH with 10 g. Zn powder gave 1.2 g. violet mixt. which was resolved by treatment with AcOH; the insol. portion consisted of 0.15 g. 5,5'-difluoroindigo, blue needles (C5H5N). The AcOH **soln.** gave violet needles of 5,5'-difluoroindirubine. VI (2.5 g.) and 50 ml. Ac2O refluxed 15 min. and the ppt. crystd. gave 2.3 g. N-acetyl-5-fluoroisatin (IX), yellow needles, m. 149.degree. (AcOH). IX (1.5 g.) and 1 g. NaOH in 30 ml. H2O refluxed 1 hr., left overnight, neutralized with dil. HCl, filtered, and acid added to pH 6 gave 0.8 g. 6-fluoro-2-hydroxycinchoninic acid, not m. below 360.degree. (AcOH). VI refluxed 12 hrs. with 20% KOH and the appropriate ketone, the solvent distd., the residue taken up in H2O, extd. with Et2O, acidified with AcOH, and the cinchoninic acid pptd. and recrystd. gave the following compds.: 6-fluoro-2-phenylcinchoninic acid (X), prepd. from PhAc, prisms, m. 223.degree. (alc.). X heated above its m.p. and distd. in vacuo gave 6-fluoro-2-phenylquinoline, prisms, m. 86.degree. (alc.); yellow picrate, m. 176.degree.. 6-Fluoro-2-(4-fluorophenyl)cinchoninic acid (XI), prepd. with p-FC6H2Ac as prisms, m. 251.degree. (alc.). XI gave 6-fluoro-2-(4-fluorophenyl)quinoline, needles, m. 128.degree. (MeOH); picrate m. 172.degree.. 6-Fluoro-2-methylcinchoninic acid, prepd. with Me2CO in H2O as needles, m. 246.degree. (H2O). 6-Fluoro-2,3-trimethylenecinchoninic acid (XII), prepd. from cyclopentanone, needles, m. 306.degree. (AcOH). XII gave 6-fluoro-2,3-trimethylenequinoline, m. 88.degree. (MeOH); picrate, m. 231.degree.. II (20 g.) condensed with 27 g. CCl3CH(OH)2 and 37 g. NH2OH.HCl as for I gave 29 g. 3,4-**difluoroisonitrosoacetanilide** (XIII), m. 156.degree. (H2O). Cyclization of 28 g. XIII with 106 ml. H2SO4 gave 14 g. 5,6-difluoroisatin (XIV), m. 226.degree. (aq. AcOH). XIV (1.7 g.) condensed with 1 g. .omicron.-(H2N)2C6H4 in 15 ml. AcOH gave 1.5 g. 8,9-difluoroindophenazine (XV), sublimable needles, m. 337.degree. (AcOH), orange-yellow color in H2SO4. Acetylation of X gave 6-acetyl-8,9-difluoroindophenazine, m. 239.degree. (AcOH), orange yellow color with H2SO4. Condensation of 3 g. III with 3 g. CCl3CH(OH)2 and 4 g. NH2OH.HCl gave 4 g. 4-bromo-3-**fluoroisonitrosoacetanilide** (XVI), m. 194.degree. (decompn.) (H2O). Cyclization of 3.5 g. XVI with 16 ml. H2SO4 gave 3 g. 5-bromo-6-fluoroisatin (XVII), orange prisms, m. 252.degree. (dil. AcOH). Pfitzinger reaction of XVII with cyclohexanone gave a cinchoninic acid, decomp. 305.degree.. Condensation of 0.5 g. XVII with 0.22 g.

.omicron.-(H2N)2C6H4 in 18 ml. AcOH gave 0.4 g. 9-bromo-8-fluoroindophenazine, m. 297.degree. (C5H5N); 6-Ac deriv., prisms, m. 251.degree. (AcOH), orange yellow coloration with H2SO4. Condensation of IV with CCl3CH(OH)2 and NH2OH.HCl gave .omicron.-**fluoroisonitrosoacetanilide** (XVIII), prisms, m. 118.degree. (aq. AcOH). XVIII with H2SO4 gave a compd. of unknown constitution, m. 281.degree. (AcOH), and none of the expected 7-fluoroisatin. Similarly, condensation of V with the same **reagents** afforded 2,4-**difluoroisonitrosoacetanilide** (XIX), m. 135.degree. (AcOH). H2SO4 treatment of XIX gave a product, prisms, m. 291.degree. (decompn.) (AcOH), which was not the correct isatin deriv. In the acridine group a route to mono- and difluoroacridines was provided by the Pfitzinger-Borsche condensation of 5-fluoro-, 5,6-difluoro-, and 5-bromo-6-fluoroisatin with cyclohexanone and 4-methylcyclohexanone to the corresponding 1,2,3,4-tetrahydroacridine-9-carboxylic acids whose thermal decarboxylation furnished the corresponding fluoroacridine bases. The following substituted 1,2,3,4-tetrahydroacridines were thus obtained (substituents and m.p. given): 7-F, 9-CO2H, 326.degree.; 7-F, 71.degree.; 2-Me, 7-F, 9-CO2H, 319.degree.; 2-Me, 7-F, 88.degree.; 6,7-F2, 9-CO2H, 336.degree.; 6,7-F2, 70.degree.; 2-Me, 6,7-F2, 9-CO2H, 341.degree.; 2-Me, 6,7-F2, 80.degree..

L20 ANSWER 11 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1959:39918 HCAPLUS
DOCUMENT NUMBER: 53:39918
ORIGINAL REFERENCE NO.: 53:7163e-i,7164a-h
TITLE: Physiologically active compounds. II. Hydrochlorides of aminoesters of substituted benzilic and glycolic acids
AUTHOR(S): Buehler, C. A.; Smith, H. A.; Glenn, D. M.; Nayak, K. V.
CORPORATE SOURCE: Univ. of Tennessee, Knoxville
SOURCE: J. Org. Chem. (1958), 23, 1432-7
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 51, 17843h. Aminoester hydrochlorides of 39 substituted benzilic and glycolic acids were **synthesized**; 2 of them appear to be more active in exptl. animals than atropine in preventing mortality from an anticholinesterase compd., and 4 of them exhibit the highest anticholinergic activity. One compd. previously reported offers some advantage over these as an anticholinergic. .beta.-Aminoethyl chlorides were prepd. by the procedures given in the previous paper. Tetrahydrofurfuryl alc. with SOCl2 gave 73% tetrahydrofurfuryl chloride (I). I, NHEt3, and NaI gave 53% N,N-diethyltetrahydrofurfurylamine (II). II was converted by HBr to 80% N-ethyl-3-hydroxypiperidine (III). III with SOCl2 gave N-ethyl-3-chloropiperidine-HCl which with aq. NaOH gave the free N-ethyl-3-chloropiperidine. The following RR'C(OH)CO2(CH2)xR''.HCl were prepd. by refluxing the proper benzilic acid with the aminoethyl chloride in dry iso-PrOH (R, R', R'', .CHI., % yield, and m.p. given): 2-MeC6H4, 2-MeC6H4, N-ethyl-3-piperidyl (IV), 0, 69, 186-7.degree.; 3-MeC6H4, 3-MeC6H4, N-ethyl-3-piperidyl, 0, 81, 150-1.degree.; 4-iso-PrC6H4, 4-iso-PrC6H4, Et4N, 2, 64, 181-2.degree.; 2-MeOC6H4, 2-MeOC6H4, Et2N, 2, 65, 171-2.degree.; 4-MeOC6H4, 4-MeOC6H4, Et2N, 2, 77, 167-8.5.degree.; 4-MeOC6H4, 4-MeOC6H4, pyrrolidino, 2, 92, 181-2.degree.; 4-MeOC6H4, 4-MeOC6H4, pyrrolidino (MeBr deriv.), 2, 53, 147-8.degree.; 2,3-(MeO)2C6H3, 2,3-(MeO)2C6H3, Et2N (V), 2, 83, 184-5.degree.; 3,4-(MeO)2C6H3, 3,4-(MeO)2C6H3, Et2N, 2, 79, 167.5-8.5.degree.; 3,4-methylenedioxyphenyl, Ph, Et2N (VI), 2, 73, 164-5.5.degree.; 3-PhC6H4, Ph, Et2N, 2, 73, 136-7.degree.; 3-PhC6H4, Ph, Et2N (VII), 2, 60, 178-9.degree.; 4-PhC6H4, Ph, piperidyl, 2, 70, 189-90.degree.; 4-PhC6H4, Ph, N-ethyl-3-piperidyl (VIII), 0, 65, 149-50.degree.; 3-PhC6H4, 3-PhC6H4, Et2N (IX), 2, 59, 158-9.degree.;

3-PhC6H4, 3-PhC6H4, piperidino, 2, 68, 197-8.degree.; 4-PhC6H4, 4-PhC6H4, Et2N, 2, 72, 183-5.degree.; 4-PhC6H4, 4-PhC6H4, piperidino (X), 2, 47, 192-3.degree.; 4-PhC6H4, 4-PhC6H4, N-ethyl-3-piperidyl (XI), 0, 74, 190-1.degree.. 2-Phenylbenzilic acid could be prepd. neither by an analogous procedure from 2-bromobiphenyl through the action of 2-biphenylmagnesium iodide on **isonitrosoacetophenone** nor through a mixed benzoin condensation of BzH and 2-PhC6H4CHO (XIa). The Grignard **reagent** of 3-bromobiphenyl (XII) reacted with N-methylformanilide to form 3-phenylbenzaldehyde (XIII) which was subjected to the benzoin condensation to give 3,3'-diphenylbenzoin (XIV). XIV was oxidized with CuSO4 in C5H5N to the corresponding benzil (XV) which on rearrangement with KOH gave 3,3'-diphenylbenzilic acid (XVI). 2,2'-Diphenylbenzilic acid could not be produced because of the failure of XIa to undergo the benzoin condensation. XII and Et phenylglyoxylate (XVII) were prepd. by known methods. XII (23.4 g.) in 300 ml. Et2O added dropwise to 2.51 g. Mg and Et2O under N, the **soln.** refluxed 2 hrs., the Grignard **soln.** added dropwise to 17.8 g. XVII in 200 ml. Et2O, the **soln.** refluxed 2 hrs., 250 ml. dil. HCl added, the Et2O layer sepd., the H2O portion extd. with more Et2O, the exts. combined, and distd. gave 18 g. Et 3-phenylbenzilate (XVIII), b1 213-18.degree.. XVIII (18 g.) in 30 ml. alc. refluxed 3 hrs. with 20 g. KOH in 100 ml. H2O, dild. with H2O, acidified, and the ppt. collected gave 11 g. 3-phenylbenzilic acid, m. 127-8.degree. (C6H6). XII (23.4 g.) in 250 ml. Et2O treated with 2.51 g. Mg, then 13.5 g. N-methylformanilide added during 2 hrs., stirred 1 hr., decompd., and sepd. gave 14 g. XIII, b2 138-44.degree.; 2,4-dinitrophenylhydrazone, m. 234-5.degree.. XIII (8 g.), 3 g. KCN, 40 ml. H2O, and 80 ml. alc. refluxed. 10 hrs., cooled, dild. with H2O, extd. with Et2O, dried, and distd. gave 6 g. orange oil. This oil, 14 g. CuSO4, 100 ml. C5H5N, and 30 ml. H2O refluxed 6 hrs., the mixt. poured onto ice and H2O, the liquid decanted, and the solid dissolved in alc. gave 2.7 g. XV, m. 119-20.degree. (MeOH); quinoxaline, m. 156.degree.. XV (8 g.) in 300 ml. Et2O left 24 hrs. with frequent shaking with 4 g. Na in 50 ml. 95% alc. and 25 ml. abs. alc., the **soln.** extd. with H2O, the aq. **soln.** extd. with Et2O, heated to 90.degree., and acidified gave 3 g. crude XVI, m. 155-7.degree. (C6H6). RR'C(OH)CO2CH2CH2NEt2.HCl (XIX) were prepd. by dissolving 0.01 mole corresponding benzilate in AcOH, hydrogenating at 3 atm. over 0.1 g. Pt catalyst until reduction was complete, removing the catalyst and AcOH, and crystg. the solid to give pure XIX. The following XIX were thus prepd. (R, R', % yield, and m.p. given): C6H11, C6H11, 72, 258-9.degree.; C6H11, C6H11, 35, 212-13.degree.; 2-MeC6H10, C6H11, 76, 165-6.5.degree.; 3-MeC6H10, C6H11, 86, 181-2.degree.; 4-MeC6H10, C6H11 (XX), 87, 190.5-2.0.degree.; 2-MeC6H10, 2-MeC6H10, 80, 163.5-4.5.degree.; 2,3-Me2C6H9, C6H11, 79, 174-5.degree.; 2,4-Me2C6H9, C6H11, 79, 155-6.degree.; 2,6-Me2C6H9, C6H11, 81, 181-2.degree.; 3,4-Me2C6H9, C6H11, 80, 177.5-8.5.degree.; 3,5-Me2C6H9, C6H11, 73, 171.5-3.0.degree.; 3-MeC6H10, 3-MeC6H10, 84, 178.5-9.5.degree.; 4-MeC6H10, 4-MeC6H10, 82, 187-8.degree.; 2,3,5-Me3C6H8, C6H11, 76, 193-4.degree.; 3,4,5-Me3C6H8, C6H11 (XXI), 90, 216.5-18.0.degree.; 3,5-Me2C6H9, 3,5-Me2C6H9, 84, 183-4.degree.; 4-iso-PrC6H10, 4-iso-PrC6H10, 84, 185-7.degree.; 3-C6H11C6H10, C6H11, 43, 133-4.degree.; 4-C6H11C6H10, C6H11, 74, 174.5-5.5.degree.; 2,3,6-Me3C6H8, C6H11, 76, 199-200.degree.. The above method was used to prep. all of the above XIX except with the di-C6H11 member in which the unreduced ester was prepd. by the method of Hill and Holmes (U.S. 2,294,770) wherein the Me ester was refluxed with the appropriate amino alc. These compds. were tested for anticholinesterase activity, blood pressure, gut, respiration, and eye effects. VII and VIII appeared to be more active than atropine in preventing mortality from an anticholesterase compd. The most active anticholinergic compds. are VI, XX, and XXI. VI and XXI are surpassed in activity by a previously prepd. compd.; this compd. has much more marked effects on blood pressure and respiration than any of the 4 new compds. Compds. effective in dilating the pupil of the eye without significant irritant action are IV, V, VI,

VIII, X, and XI. 3-PhC6H4CPh(OH)CO2(CH2)2NEt2.HCl and IX, which resemble V and VI in being diethylaminoethanol derivs., are as active as the latter 2 compds. in dilating the pupil, but are definitely irritating.

L20 ANSWER 12 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1956:12302 HCAPLUS
DOCUMENT NUMBER: 50:12302
ORIGINAL REFERENCE NO.: 50:2561b-i,2562a-f
TITLE: The rearrangement of 2-acetyl- and 2-benzoylcoumarone oxime p-toluenesulfonates
AUTHOR(S): Geissman, T. A.; Armen, Ardy
CORPORATE SOURCE: Univ. of California, Los Angeles
SOURCE: J. Am. Chem. Soc. (1955), 77, 1623-7
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB The rearrangement of the tosylate (I) of 2-acetylcoumarone oxime (II) to 2-methyl-3-chromonol (III) (cf. Vargha, et al., C.A. 44, 2973d) has been confirmed. A structure for the so-called acetal (IV) formed in the reaction has been proposed; it appears likely that IV has structure V. The rearrangement of 2-benzoylcoumarone oxime (VI) tosylate (VII) yielded flavonol (VIII) and 2-benzoyl-3-coumaranone (IX). New **syntheses** have been described for 2-acylcoumaranones; and 3-acetyl-2-coumaranone (X) has been described for the 1st time, correcting an earlier report of its prepn. by Pfeiffer and Enders (C.A. 45, 9046d). I prepd. and treated with MeOH by the method of Vargha, et al. (loc. cit.), yielded III, m. 179-81.degree., and IV, b4 122-7.degree., nD25 1.5142. Dry Me2CO (100 cc.), 75 g. K2CO3, 50 g. o-HOC6H4CO2Me, and 30.4 g. AcCH2Cl heated 5 hrs. on the steam bath, the mixt. cooled, dild. with H2O, and extd. 3 times with Et2O, the aq. phase acidified, and the cryst. ppt. (8.0 g.) recrystd. from ligroine and dil. EtOH gave 2-acetylcoumaranone (Xa), m. 90-1.degree.; it gave an olive-green color with FeCl3 in dil. aq. NaHCO3; an Et2O **soln.** treated with Cu(OAc)2 gave a Cu complex; it gave a blood-red 2,4-dinitrophenylhydrazone. o-HOC6H4COCH2Ac (XI) (2.0 g.) in 200 cc. CHCl3, contg. 2 g. K2CO3 treated dropwise with stirring at 0.degree. with 1.8 g. Br in 40 cc. CHCl3, the colorless mixt. kept 0.5 hr. at 0.degree., refluxed 1 hr., filtered, and extd. with 5% aq. Na2CO3, and the aq. ext. acidified yielded 0.81 g. Xa, colorless crystals, m. 90-2.degree.. Xa treated with Ac2O and pyridine gave the acetate, m. 86-7.degree.. 2-Methylchromone (3.1 g.) (prepd. by the acid-catalyzed ring closure of XI) in 30 cc. C6H6 hydrogenated 22 hrs. at atm. pressure over 3.1 g. Pd-CaCO3, the mixt. filtered and evapd., the residual oil dissolved in 60 cc. abs. EtOH, 6 cc. AcOH, and 6 g. Girard **reagent** T, the **soln.** refluxed 1 hr., cooled, treated with 250 cc. ice cold H2O contg. 3.6 g. Na2CO3, the **soln.** extd. with Et2O, made 0.5N in HCl, kept 1 hr. at room temp., and extd. with Et2O yielded 1.74 g. VI. VI (0.74 g.) in 35 cc. boiling 95% EtOH treated alternately with shaking portionwise with 4.0 cc. AmONO and 20 cc. concd. HCl, the **soln.** allowed to stand 2 hrs., dild. with 100 cc. H2O and cooled gave 0.52 g. III, m. 178-80.degree.; it gave a violet-blue color with FeCl3. VI treated with AmONO under alk. conditions followed by hydrolysis of the intermediate **isonitroso** deriv. gave a somewhat poorer yield of III. IV (240 mg.) in 10 cc. EtOH and 10 cc. 2N H2SO4 refluxed 2 hrs. did not give any III, but the mixt. refluxed 3 days and then cooled gave 60 mg. III. IV did not give CHI3 with NaOI, nor CHBr3 with NaOBr. IV (0.50 g.) in 15 cc. 48% HBr heated 1 hr. at 120.degree., the **soln.** cooled, dild. with 100 cc. H2O, and extd. with Et2O, the ext. shaken with N aq. NaOH, the basic **soln.** filtered and acidified, and the ppt. recrystd. from dil. EtOH gave 0.13 g. 2-methylcoumarone-3-carboxylic acid (XII), m. 190-1.degree. (from aq. EtOH). o-HOC6H4CH2CO2H (1.5 g.) and 4 cc. Ac2O heated 0.5 hr. in 30 cc. pyridine on the steam bath, the mixt. cooled, dild. with dil. HCl, and

again cooled, the resulting solid (0.95 g.) dissolved in aq. NaHCO3, the **soln**. decolorized with Norite, filtered, and acidified, and the colorless ppt. recrystd. from aq. EtOH gave X, m. 133-4.degree.; it gave a deep blue color with FeCl3. X treated with CH2N2 in Et2O gave the Me ether, m. 125-6.degree.. X treated 2 hrs. with Ac2O and NaOAc gave the acetate, m. 114-16.degree.. Isocoumaranone (0.53 g.) in 10 cc. dry EtOAc treated with 0.10 g. NaH, the mixt. refluxed 1 hr., cooled, treated with 20 cc. dil. HCl, the Et2O layer extd. with aq. NaHCO3, and the aq. alk. ext. acidified gave 0.30 g. colorless compd., m. 155-6.degree., probably 3-o-hydroxy-phenylacetylisocoumaranone; it gave a deep blue color with FeCl3. 2-Methylcoumarone (13 g.) was converted to the 3-Br deriv. (XIII), b6 100-4.degree., nD20 1.5870. XIII (0.50 g.) in 10 cc. Et2O added at -78.degree. to 8 cc. 0.32M BuLi in 15 cc. Et2O, the mixt. treated after 2 min. with excess Dry Ice, warmed to room temp., and dild. with H2O, the Et2O layer washed twice with aq. NaHCO3, and the aq. ext. acidified gave XII, m. 190-1.degree.. 2-Benzoylcoumarone (20 g.) refluxed 2 hrs. with 18.8 g. NH2OH.HCl and 50.5 g. KOH in aq. EtOH, the mixt. dild. with H2O and cooled, and the cryst. deposit recrystd. from aq. AcOH gave 18.2 g. VI, m. 128-9.5.degree.. p-MeC6H4SO2Cl (XIV) (0.46 g.), 0.50 g. VI, and 1 cc. dry pyridine kept 1 hr. at room temp., the mixt. dild. with Et2O, the Et2O **soln**. washed 3 times with dil. H2SO4, twice with 2N NaOH, and twice with H2O, dried, and evapd. to dryness in vacuo at room temp., the oily residue dissolved in EtOH, and the **soln**. dild. to beginning crystn. gave VII, m. 109-10.degree.. VII (14.35 g.), m. 102-5.degree., gave in an attempted recrystn. from hot aq. EtOH coumarilanilide (XV), m. 151-4.degree.; the aq. alc. mother liquor extd. with Et2O, the ext. washed with dil. aq. NaOH, and the alk. **soln** . acidified gave 0.33 g. VIII, m. 167-8.degree.. Crude VII from 10 g. VI and 9.2 g. XIV in 20 cc. dry pyridine in Et2O **soln**. dild. with 200 cc. 80% aq. MeOH, the Et2O distd. off, the residual **soln**. refluxed 2 hrs., cooled, and extd. with Et2O, the ext. washed with 5% aq. NaHCO3, and the aq. alk. washing acidified yielded 40 mg. IX, m. 79-80.degree. (from aq. EtOH); it gave an olive-green color with FeCl3; the remaining Et2O **soln**. extd. with dil. aq. NaOH, and the alk. ext. acidified yielded 1.1 g. VIII, m. 166-7.degree. (from EtOH); the residual Et2O **soln**. dried and evapd., and the partially cryst. material (9.0 g.) recrystd. from EtOH gave 2.05 g. XV, m. 155-6.degree.; the EtOH mother liquor extd. with Et2O, a 50-cc. aliquot of the ext. (250 cc.) evapd., and the residual oil (1.15 g.) sapond. gave 0.27 g. coumarilic acid, m. 190-1.degree.; the residue from another 50-cc. aliquot distd. at 6 mm. and the resulting cryst. distillate (0.30 g.), b. below 190.degree., recrystd. from dil. EtOH gave Me coumarilate, m. 51-2.degree.. o-HOC6H4COCH2Bz (0.65 g.) and 0.8 g. dry K2CO3 in 50 cc. CHCl3 treated with stirring at 0.degree. with 0.44 g. Br in 10 cc. CHCl3, the mixt. refluxed 1 hr., cooled, and washed with N NaOH, the aq. alk. washings acidified, and the resulting ppt. recrystd. from aq. EtOH gave 0.37 g. 2-benzoylcoumaranone, m. 79-80.degree.; it gave an olive-green color with FeCl3.

L20 ANSWER 13 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1955:15979 HCAPLUS
DOCUMENT NUMBER: 49:15979
ORIGINAL REFERENCE NO.: 49:3153h-i,3154a-i,3155a-i,3156a-i,3157a-i,3158a-b
TITLE: Attempted synthesis of penicillins
AUTHOR(S): Bachmann, W. E.; Cronyn, M. W.
CORPORATE SOURCE: Univ. of Michigan, Ann Arbor
SOURCE: Chem. of Penicillin (H. T. Clarke, et al.)(Princeton Univ. Press) (1949) 849-91
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB In the studies of the **synthesis** of penicillin, many of the procedures which involved a cyclization in the final step were

theoretically capable of yielding either the .beta.-lactam or oxazolone-thiazolidine structures. Tests for antibiotic activity were employed as criteria of the potential usefulness of a reaction but no activity greater than 1-2 units per mg. (0.1% activity) was ever observed. Representative attempts to activate penicilloic acids are reported. In these numerous azlactonizing expts. the agents used included Ac2O, Ac2O in pyridine, acid chlorides, phosphorus trihalides, POCl3, PCl5, azlactones, and aroyl azides. Various dehydrating agents and adsorbents such as CaCl2, CuSO4, P2O5, Al2O3, silica gel, Nuchar, etc., were also tried. Control expts. to det. the stability of benzylpenicillin or its .beta.-ester under these operating conditions were performed. Benzylpenicilloic acid, PhCH2CONHCR(CO2H)CH.S.CMe2.CH(CO2H).NH (I, R = H) (Ia) and its esters in the form of racemic mixts. or of optically active isomers and various homologs and analogs were employed. These expts. are classified and tabulated. The few products isolated and characterized proved to be penicillenates formed by cleavage of the thiazolidine ring after azlactonization, the extent of which was detd. by difference from the yield of .alpha.-benzylamide. To prevent formation of penicillenates, it was planned to use 6-alkylpenicilloic acid derivs. (I, R = alkyl), but no such compds. were available. Similar blocking attempts by utilizing the benzyl thioamide (instead of the amide) and .alpha.-thio ester derivs. of penicilloic acids failed to yield antibiotic active compds. Procedures designed particularly to produce compds. with the .beta.-lactam structure included the action of Grignard **reagents** on .alpha.-alkyl and dialkylpenicilloates. Treatment of benzylpenicilloic acid .alpha.-ester with BuMgBr, carbonation, and pyrolysis of the product at 210-50.degree. produced inactive material. Although .beta.-methyl-D-.gamma.-benzylpenicilloate (Ib) treated with PBr3 in dioxane gave a product with a 5.6 .mu. bond in the infrared, characteristic of the .beta.-lactam CO group, attempts to isolate the active material by treatment of the mixt. with CH2N2 or bases were unsuccessful. Various attempts to form the .beta.-lactam structure by elimination of CO2, CO, N, etc., from 5-8 membered rings produced by the closure of suitably substituted penicilloates were unsuccessful, as were efforts based on the elimination of the elements of BzH, NaBr, etc., from similar compds. Prepn. of active compds. was attempted from .alpha.-amides, .alpha.-hydrazides, and N4-acylpenicilloates. A mixt. of benzylpenicilloic acid .alpha.-amide (Ic) (401 mg.) and 156 mg. BF3.Et2O complex in 10 ml. dioxane was heated to 100.degree. without sepn. of the BF3.NH3 complex, indicating no reaction. Similarly, cyclization of the HCl salt by heating alone or in solvents could not be accomplished Attempts to form a triazine and to arrive at the .beta.-lactam by thermal decompn. were made by converting Ic to the .alpha.-amido-N-nitroso compd., transformed by treatment with NaOH in dioxane or KOH in MeOH to a compd., m. 133-4.degree., [.alpha.]D23 16.degree. (c 0.49%, EtOH). No antibiotic activity resulted from the thermal treatment of this "triazine" nor was any significantly active material obtained from the product of the nitrosation of the .alpha.-hydrazides of the .beta.-esters of benzyl- and phenylpenicilloic acids. Dropwise treatment of 36.6 g. .alpha.-methyl D-benzylpenicilloate (II) in 50 ml. CHCl3 contg. 8 ml. pyridine with 10 ml. Me2CHCOCl with stirring at room temp. yielded 45 g. .alpha.-Me N-isobutyryl-D-benzylpenicilloate; .alpha.,.beta.-di-Me ester, m. 123-4.degree., hydrolyzed by NaOH in aq. MeOH to the .beta.-Me ester, m. 206-7.degree.. Formylation of II produced an amorphous N4-formyl deriv. No active material was obtained on pyrolysis of these N4-derivs. Pyrolysis of .alpha.-Et .beta.-Me N4-acetyl-N8-methyl-9-phenylpenicilloate gave a compd. with slight antibiotic activity, but none was obtained by the pyrolysis of the monoester or the corresponding N4-isobutyryl compds. The prepn. of benzylpenicillin with the .beta.-lactam structure was attempted by cyclization of di-Me N-carbophenoxy-D-benzylpenicilloate (III) by the Dieckmann procedure. III (125 mg.) in 3 ml. Et2O and (ClCH2)2 was added with stirring to 2 equivs. Me2CHMgI in 3 ml. Et2O. Decompn. of the gummy complex with 2N H2SO4 gave 80% unchanged III and a small yield of gum

which, on sapon. in pyridine, showed no antibiotic activity. Similarly, the di-Me ester of N4-methoxalylbenzylpenicilloic acid failed to cyclize on treatment with NaOMe, Ph3CNa, BF3, or Me2CHMgBr. Possible prepn. of compds. with the .beta.-lactam structure from cyclization of N-(N-phenylacetyl- .beta.,.beta.-diethoxyalanyl)penicillamine (IV) was early envisaged. In the prepn. of IV, direct formylation of the Et ester of phenaceturylpenicillamine by the action of HCO2Et and Na was unsuccessful. Addn. of 0.523 g. NaNO2 in H2O to 4 g. benzylpenaldic acid di-Et acetal hydrazide in 2N HCl at 0.degree. gave the gummy azide, which was coupled with 1.374 g. penicillamine (V) HCl salt by stirring with 0.80 g. Na2CO3 and 0.637 g. NaHCO3 in 15 ml. H2O 2 hrs. and recrystg. from aq. EtOH to give colorless needles of IV, m. 67.degree.. Similar condensation of the azide from benzylpenaldic acid di-Me acetal hydrazide, m. 180.degree. with D-V.HCl gave N-(N-phenylacetyl-.beta.,.beta.-dimethoxyalanyl)-D-penicillamine (VI), m. 115-16.degree., [.alpha.]D25 24.degree. (c 1.0, MeOH); Me ester, m. 96.degree., [.alpha.]D25 36.degree. (c 0.1, MeOH). Condensation of the azide from .alpha.-phenylacetamide-.beta.,.beta.-dimethoxypropionic acid hydrazide with V Me ester produced a "urea," m. 122-3.degree., [.alpha.]D25 -27.degree. (c 1,0, MeOH) which evolved H2S on heating at 100.degree. in Ac2O to yield an inactive compd., m. 151-2.degree.. VI showed considerable thermal stability and fusion alone at 150.degree. or with pyridine-HCl at 140.degree.; these fusions gave material with 0.2-0.5 unit activity per mg. Ring closures of the ester were attempted. Treatment of 2-phenyl-4-ethoxymethylene-5-oxazolone in 2N HCl with abs. EtOH 2 days at room temp. produced N-benzyl-.beta.,.beta.-diethoxyalanine Et ester, m. 48.degree.; hydrazide (VII), m. 154-5.degree., converted by warming at 100.degree. for 1 hr. with 2N HCl and EtOH to 2-benzoylamino-3-pyrazolone, m. 200-1.degree.. Condensation of the azide from VII with V.HCl gave N-(N-benzoyl-.beta.,.beta.-diethoxyalanyl)penicillamine (VIII), m. 150.degree.; Me ester, m. 90-1.degree., not cyclized by cold Ac2O nor by hot pyridine or Ac2O. Condensation of 20 g. of D-V Me ester-HCl and 22 g. 2-benzyl-4-methoxymethylene-5-oxazolone in 100 ml. pyridine by the addn. of 100 ml. MeOH gave a compd. (IX), m. 140-1.degree., [.alpha.]D22 100.7.degree. (c 1.45, MeOH) and N-(.alpha.-phenylacetylamino-.beta.-methoxyacrylyl)penicillamine Me ester, m. 108.9.degree., transformed by refluxing with Et2O to IX, which gave a neg. test for sulfhydryl group, and was hydrogenolyzed over Raney Ni to .beta.-methoxy-N-phenylacetylalanyl-D-valine Me ester, m. 86-7.degree., identical with a **synthetic** prepn. Heating IX 2 hrs. in pyridine at 78-80.degree. or in xylene 16 hrs. with a trace of Et2NH gave material with no antibiotic activity. Attempts to effect cyclization of penicillenates with the formation of a thiazolidine ring were fruitless. No antibiotic activity resulted when Me benzyl- or amylpenicillenates were kept in pyridine at room temp. 1 day or on treating the crude penicillenates from the condensation of V and 2-benzyl-4-alkoxy-5-oxazolones with toluene alone or with ascaridole, BzO2H, N-ethylpiperidine, Ib, or by treatment with pyridine and Cu(OAc)2. Various attempts to isomerize penillic to penicillenic acids by ultraviolet radiation, AlCl3 in dioxane, Al(OBu-tert)3 in dioxane, pyridine with ascaridole and with BzO2H, various acids in (ClCH2)2, BF3, and PhNCO failed to bring about the reversal. Treatment of the oxazole-thiazolidine, N: CPh.O.CCl:CCH.S.CMe2.CH(CO2H).NH , with dry pyridine at 60.degree. for 5 hrs. yielded antibiotically active material (0.25-0.5 units per mg.), quickly inactivated by the action of penicillinase. Condensation of 2-benzyl-4-oxazolecarbonylchloride and V Me ester gave an acylpenicillamine deriv. Portions (3 ml.) of a mixt. of 468 mg. of Me D-5,5-dimethyl-2-thiazoline-4-carboxylate (X) and 444 mg. 2-benzyl-5-oxazolone in 9 ml. toluene were refluxed, and heated at 100.degree. and at 65-70.degree. for 10-min. periods. Samples of the reaction products were sapond. and assayed in vitro but showed no activity. No biol. activity was found in products obtained from the condensation of equimolar quantities of 2-phenyl- or 2-amyl-5-ethoxyoxazole with X. To provide a necessary acylaminoketene for reaction

with X to produce a compd. with .beta.-lactam structure, 2.64 ml. PhCH2COCl was added to a suspension of Hg2(NCO)2 in 15 ml. dry benzene and the filtered **soln.** was satd. with dry HCl to give presumably PhCH2CONHCOCl, m. 105-8.degree. (phenylacetylurea, m. 209-10.degree.). Treatment with excess CH2N2 gave presumably PhCH2CONHCOCHN2, which was rearranged with Ag2O to PhCH2CONHCHC:O in the presence of X to yield biologically active but not reproducible products. A large no. of investigations were concerned with the prepn. of "dehydropenicillins" of the structure N:C(CH2Ph).O.CO.CHC:N.CH(CO2H).CMe2.S, or N:C(CH2Ph).O.CO.C:C.NH.CH(CO2H).CMe2.S (XI), which would give the oxazolone-thiazoline structure on reduction. Refluxing 15 g. NaH4.H2O with 20.7 g. PhCH2CONHCH2CO2Me in 50 ml. MeOH 1 hr. and recrystg. the product from Me2CHOH yielded phenaceturyl hydrazide, m. 130-2.degree., converted to the azide, m. 85-6.degree., which was condensed with V.HCl to crude D-N-phenaceturylpenicillamine, m. 137-40.degree.. Cyclization by standing for 5 days in satd. ethereal HCl gave a product whose analysis corresponded to that of dehydrobenzylpenilloic acid-HCl (XII). Simultaneous addn. of 125 g. PhCH2COCl and 32 g. NaOH in H2O below 0.degree. to 100 g. of H2NCH2CN.H2SO4 in 500 ml. H2O contg. 52 g. NaOH yielded 70 g. phenylacetamidoacetonitrile, m. 93, converted by treatment with dry HCl at 0.degree. in dioxane and MeOH to phenylacetamidoacetimino Me ether-HCl, m. 158.degree. (Et ether-HCl, m. 165.degree.), yielding with excess Na2CO3 in Et2O the corresponding ethers (Me, m. 80-1.degree.; Et, m. 91-2.5.degree.). Condensation of either of these ethers with V Me ester-HCl gave XII Me ester, b0.1 180-90.degree., reduced in Et2O over Al-Hg to Me benzylpenilloate (HCl salt, m. 85-95.degree.), cleaved by HgCl2 to benzylpenilloaldehyde, identified by the 2,4-dinitrophenylhydrazone, m. 195-8.degree.. A mixt. of 1.8 g. H2NCH(CO2Et)2 in 25 ml. Et2O and 1.5 g. Na2CO3 in 10 ml. H2O was shaken and 1.5 g. PhCH2COCl was added dropwise; warming to complete reaction and sepg. the Et2O layer gave di-Et phenylacetamidomalonate, m. 67-8.degree.. Treatment of 1.08 g. of this ester in 5 ml. EtOH contg. 0.21 g. KOH, evapn. to dryness, **soln.** in H2O, acidification and recrystn. from CHCl3-petr. ether produced mono-Et phenylacetamidomalonate, m. 104-5.degree.. This half-ester was converted to the hydrazide, m. 143-5.degree., and then to the colorless cryst. azide, which was filtered off and added to V.HCl in aq. Na2CO3. After 15 min. the mixt. was acidified with HCl to yield N-(N-phenylacetyl-.alpha.-carboxyglycyl)penicillamine, m. 152-3.degree.. The compd. appeared to react with ethereal HCl but no cryst. products were isolated. Similarly, the monoazide of benzoylaminomalonic acid was coupled with V and its Me ester without production of cryst. material. No definite products were obtained from N-phenaceturylpenicillamine Me ester and CH(OEt)3, HCSNH2 or CHCl3. Another approach employed 2-benzyl-4-carbethoxy-5-oxazolone (XIII). Phenylacetamidomalonic acid ester hemihydrate (1 g.) was warmed on the steam bath 30 min. with 10 ml. Ac2O, freed from excess **reagent** in vacuo, and distd. in vacuo at 50-60.degree. gave PhCH2CONHCH2CO2Et, m. 79-80.degree.. XIII reacted readily with PhNH2 and p-H2NC6H4Me to produce phenylacetamidomalonanilic Et ester, m. 156.degree., and the corresponding toluidide Et ester, m. 157-8.degree.. Addn. of 1 g. crude XIII to 500 mg. of cysteine Me ester in 15 ml. benzene and 5 ml. AcOEt and recovery of the residue from Et2O gave N-(N-phenylacetyl-.alpha.-carbethoxyglycyl)cysteine Me ester, m. 106-20.degree.. Similarly, allowing a mixt. of XIII and V Me ester to stand in Et2O overnight, extg. with 2N HCl and aq. Na2CO3, concg. the Et2O ext. and recrystg. the residue from CHCl3-petr. ether gave N-(N-phenylacetyl-.alpha.-carbethoxyglycyl)penicillamine Me ester, m. 128-9.degree., not convertible into the thiazolidine by ethereal HCl. The hippuryl analog similarly failed to cyclize in methanolic HCl. The desired "dehydropenicillin" was successfully **synthesized** from 2-carbethoxymethyl-4-carbomethoxy-5,5-dimethylthiazoline (XIV); this with benzenediazonium chloride gave the phenylazo deriv., m. 120.degree.. V Me ester (3.2 g.) in 5 ml. CH2(CO2Et)2 was added dropwise to 10 ml.

C2H(CO2Et)2 at 175.degree.. After distn. in vacuo the residual oil was distd. at high vacuum, yielding 2.5 g. XIV, b0.018 156.degree., m. 109-11.degree.. XIV (10.2 g.) in 75 ml. EtOH and 75 ml. 2N HCl was treated dropwise with stirring with 5.0 g. NaNO2 in 20 ml. H2O at 0.degree.. After 15 min., the mixt. was dild. with H2O to yield 2-**isonitrosocarbethoxymethyl**-4-carbomethoxy-5,5-dimethylthiazoline, m. 141.degree.. Warming 0.4 g. of nitroso compd. in 8 ml. 2N NH4OH for 5-10 min. on the steam bath with 1.2 g. Na2S2O4 in 5 ml. H2O gave 2-aminocarbethoxymethyl-4-carbomethoxy-5,5-dimethylthiazoline (XV).HCl, m. 163-7.degree.. Phenylacetylation of 1.8 g. XV oxalate by stirring for 2.5 hrs. with 25 ml. Et2O, 1.5 g. NaHCO3, and 0.8 g. Ph2CH2COCl yielded 4-carbomethoxy-5,5-dimethyl-2-phenylacetamidocarbethoxymethylthiazoline (XVI), m. 136-7.degree. (.alpha.-Et .beta.-Me "benzyldehydropenicilloate"). Treatment of 0.6 g. XVI in 10 ml. EtOH with 3.06 ml. 0.51 N NaOH for 1 hr. and acidification of the filtrate with 1 equiv. 0.5N HCl at 0.degree. produced 4-carboxy-5,5-dimethyl-2-phenylacetamidocarbethoxymethylthiazoline, m. 120-4.degree. (decompn.); morpholine salt, m. 173.degree., by preferential hydrolysis of the .beta.-ester group. Refluxing 15 g. XVI gently with 220 ml. CHCl3 and 8.5 g. PCl5 50 min., allowing to stand at room temp. several hrs., washing with aq. NaHCO3, chromatographing over Al2O3, and recrystg. from CHCl3-petr. ether yielded 7.5 g. "thiazolineoxazolone" (XVII, R = PhCH2), m. 118-19.degree.. The same compd. was produced from the corresponding .alpha.-benzyl .beta.-Me ester (XVIII) by loss of the elements of PhCH2OH. This remarkable formation of oxazolones rather than oxazoles by ring formation suggests that the precursors may have the structure RCONHC(CO2R'):C.S.CMe2.CH(CO2R").NH, and yield by loss of the elements of R'OH compds. such as XVII. The p-nitrobenzamide analogs of XVII and XVIII and the corresponding compds. of the caproamido series were similarly prepd., providing the following compds.: 4-carbomethoxy-5,5-dimethyl-2-p-nitrobenzamidocarbethoxymethylthiazoline (XIX), m. 173.degree.; 4-carboxy acid, m. 112.degree., remethylated to XIX. Shaking 4.23 g. XIX with 39.4 g. 0.51N NaOH 15 hrs., acidifying the filtrate at 0.degree., and purification through the Pb salt by decompn. with H2S gave 4-carboxy-5,5-dimethyl-2-p-nitrobenzamidomethylthiazoline, m. 110.degree. (softening). Refluxing 0.8 g. XIX in 15 ml. dry CHCl3 with 1 g. PCl5 1 hr. and chromatographing over Al2O3 yielded yellow prisms of 4-(4-carbomethoxy-5,5-dimethylthiazolin-2-yl)-5-ethoxy-2-(p-nitrophenyl)oxazole, m. 205.degree.. Cyclization of XIX by refluxing in CHCl3 over PCl5, chromatographing the washed CHCl3 **soln.** over Al2O3, and recovering material from the upper part of the column gave XVII (R=p-O2NC6H4) (XX), m. 265.degree.. Caproylation of XV oxalate yielded 4-carbomethoxy-5,5-dimethyl-2-caproamidocarbethoxymethylthiazoline (XXI), m. 104-5.degree.; 4-carboxy acid, m. 149-50.degree.. Cyclization of XXI produced XVII (R = Am) (XXII), m. 87-8.degree.. Heating 30 ml. NCCH2CO2Et with 150 ml. PhCH2OH at 194-200.degree. for 3 hrs. and removal of the residual PhCH2OH at 100.degree. and 18 min. yielded 34 g. NCCH2CO2CH2Ph, b0.5 141.degree., nD19 1.5206. A mixt. of 17.5 g. ester and 4.6 g. anhyd. EtOH was treated with 3.8 g. dry HCl overnight, yielding 23.5 g. carbobenzyloxyacetimino Et ether-HCl, m. 89.degree. (effervescence). Condensation of 5.1 g. HCl salt with 4.0 g. V Me ester, 2.5 g. AcOK, 5 ml. H2O, and 5 ml. Et2O by shaking together 2 hrs. yielded 3 g. 4-carbomethoxy-5,5-dimethyl-2-carbobenzyloxymethylthiazoline, m. 78.degree., converted to the oily 2-**isonitroso** deriv., reduced over HgAl in EtOH, and crystd. Me2CO-Et2O in Et2O to give 12.8 g. 4-carbomethoxy-5,5-dimethyl-2-aminocarbobenzyloxymethylthiazoline; oxalate (XXIII), m. 120-1.degree., phenylacetylated to XVIII, m. 132-3.degree.; caproylated to the 2-caproamido deriv. (XXIV), m. 115.degree., and p-nitrobenzoylated to the 2-p-nitrobenzamido compd. (XXV), m. 182-3.degree.. XVIII was sapond. to the 4-carboxy acid (XVIIIa), m. 153-4.degree.. Cyclization of XVIII, XXIV, and XXV produced the "thiazoline-oxazolones" XXII, XX, and XVII. Cyclization of XVIIIa gave a "thiazoline-oxazolone" acid (XXVI), m. 190.degree. (hemihydrate, m.

122-3.degree. (decompn.); HCl salt, m. 165.degree. (decompn.)) also obtained by hydrolysis of XVII. Methylation of XXVI with excess CH2N2 in ether gave the stereoisomeric N4-Me derivs. of the .beta.-Me esters, m. 151-2.degree. and 110-111.degree.. Many attempts were made without success to reduce XXV and the caproamido analog XXII and their Me esters to the penicillins or their esters. No appreciable biol. activity developed and vigorous reduction led by breakdown to unidentified products. In another procedure 13.3 g. PhCHClCOCl was added dropwise with cooling and stirring to 12 g. .beta.,.beta.-diethoxyalanine in 150 ml. N NaOH. After extn. with CHCl3, the aq. layer was acidified with 2N H2SO4, the oily product was taken up in Et2O, dried, and heated with excess CH2N2 in Et2O. Distn. in high vacuum gave 12.6 g. pure Me .alpha.-chlorobenzylpenaldate di-Et acetal, m. 72-4.degree.; 2,4-dinitrophenylhydrazone, m. 153-4.degree..

Heating 3.3 g. acetal in 7 ml. glacial AcOH with 1.5 g. V.HCl.H2O 30 min. and pptn. with 150 ml. dry Et2O gave 2.83 g. .alpha.-Me DL-(.alpha.-chlorobenzyl)penicilloate-HCl, sintering at 95.degree., decomp. at 180.degree.. Treatment of 10.52 g. HCl salt with 69.3 ml. N NaOH overnight and neutralization at 0.degree. with 46.2 ml. N HCl yielded 5.2 g. DL-chlorobenzylpenicilloic acid, m. 85-90.degree. (decompn.), converted by shaking with 10.8 g. pyridine and 35.2 ml. Ac2O to "benzyldehydropenicillin," m. 90-5.degree. (decompn.), with the probable structure PhCH:C.O.CO.CMe:N. All attempts at reduction failed. None of the expts. performed yielded penicillin. No active products were obtained from the action of phenylketene di-Me acetal on D-4-carbomethoxy-5,5-dimethyl-.alpha.-amino-2-thiazolidineacetic acid (XXVII) or of PhCCl3 on the Na salt of XXVII in the presence of NaHCO3, NEt3, or pyridine. The reaction of COCl2 with XXVII gave a bicyclic product (XXVIII), m. 168-9.degree. (decompn.), [.alpha.]D23 215.degree. (EtOH), which was heated with PhCH2MgCl in the hope that the Grignard product would undergo cyclization to penicillin Me ester. However, no activity was found in the reaction product. Since XXVIII was shown to have an active H atom, the use of MeCH2CH:CHMgBr was later proposed (C.A. 39, 2968.2).

L20 ANSWER 14 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1945:25415 HCAPLUS
DOCUMENT NUMBER: 39:25415
ORIGINAL REFERENCE NO.: 39:4059h-i,4060a-b
TITLE: The synthesis of 1,2-cyclohexanedione dioxime (nioxime)
AUTHOR(S): Rauh, Everett G.; Smith, G. Frederick; Banks, Charles V.; Diehl, Harvey
SOURCE: J. Org. Chem. (1945), 10, 199-204
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB The various methods for the prepn. of 1,2-cyclohexanedione dioxime (nioxime) (I) which, because of its H2O soly., may be a useful analytical **reagent** for Ni, are checked. According to the method of Riley, et al. (C.A. 24, 4305) 280 g. SeO2 in 1500 cc. 95% EtOH is added at 70-80.degree. to 250 g. cyclohexanone (II) over a period of 2 hrs. and refluxed for an addnl. 2 hrs. The EtOH is distd. off, the residual liquid (III) decanted from the Se, the latter washed with ether, the ether evapd., and the residue added to III. Distn. of III at 25 mm. gives 200 g. of a mixt. of II, 1,2-cyclohexanedione (IV), and H2O. The mixt. is dild. with 1 l. ether and extd. with ice-cold 10% KOH, and the alk. ext. is washed with ether, acidified with ice-cold HCl, and extd. with ether. The dried ether ext. when distd. gives 55 g. IV, b25, 96-7.degree.. When to 55 g. IV and 170 g. H2NOH.HCl (V) in 500 cc. H2O, cooled to 0.degree., an ice-cold **soln**. of 225 g. KOH in 1 l. H2O is added dropwise with stirring, the mixt. heated for 2 hrs. on a steam bath, cooled to 0.degree., neutralized with CO2, and satd. with NaCl, 70% I, m. 187-8.degree. (decompn.), is obtained. The **synthesis** of I via

the 2-**isonitrosocyclohexanone** (VI) prepd. according to Jaeger and van Dijk (C.A. 30, 6341.7) failed. VI is, however, obtained in 81.6% yield according to a modified method of Pezold and Shriner (C.A. 27, 274). To a stirred mixt. of 1 l. alc. EtONa (from 46 g. Na) and 700 cc. ether, cooled to -10 to -15.degree., a mixt. of 200 g. II and 350 g. 2-ethylhexyl nitrite in 2.5 l. anhyd. ether is added over a period of 40 min. Stirring is continued for 3 hrs. and the Na salt (VII) of VI is filtered and washed with ether. When 104 g. V in 2 l. MeOH is added to 149 g. VII in 1 l. MeOH and the mixt. refluxed for 24 hrs., I, m. 189-90.degree., is obtained in an over-all yield of about 30%.

L20 ANSWER 15 OF 16 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1930:32816 HCAPLUS
DOCUMENT NUMBER: 24:32816
ORIGINAL REFERENCE NO.: 24:3488g-i,3489a-i,3490a-i,3491a-i,3492a-e
TITLE: Dioximes. LXI
AUTHOR(S): Ponzio, G.
SOURCE: Gazz. chim. ital. (1930), 60, 49-96
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C. A. 24, 1032-3. A crit. review and discussion of past work on dioximes by various investigators leads to the following generalizations concerning the formation of various types of derivs. from different types of glyoximes, and the structure of the latter: (1) among almost all sym. and asym. glyoximes there is a form in which only 1 of the two NOH groups has a H atom capable of substitution by Ni, Cu or Co, i. e., a form which, treated with Ni, Cu or Co **soln.**, yields a complex salt deriv. from 2 mols. of glyoxime by substitution of 2 oximic H atoms with a Ni, Cu or Co atom; (2) representing these metal (M) complexes by the formula (DH)2M (where DH is the univalent residue resulting from the removal of oximic H from a glyoxime DH2), the forms of some sym. and asym. glyoximes which give complex salts can also add (in the absence of water) a mol. of metal halide with formation of addn. compds.; (3) the forms of sym. and asym. glyoximes from which the complex (DH)2M salts are derived react (in the presence of water) with metallic Ni, Cu or Co, with evolution of H and formation of the same complex salts; (4) all of the sym. and asym. glyoximes form O-monoethers and O,O-diethers, and some form also N-monoethers, N,O-diethers and N, N-diethers; (5) among some asym. glyoximes there is a form from which, by substitution of the oximic H by a NO2 group, pseudonitroloximes are formed; (6) among some asym. glyoximes there is a form from which, by elimination of 1 mol, of H2O, nitrosoisoxazoles are formed; (7) among some asym. glyoximes there is a form in which only 1 of the 2 oximino groups has the H atom capable of substitution by Ac; (8) only 1 of the two NOH groups can be eliminated (in the form of NH2OH) from asym. glyoximes, with formation of 1 of the 2 monooximes of the corresponding 1,2-di-C: O compd., and (9) the majority of the sym. and asym. glyoximes can be dehydrogenated by oxidizing agents (in neutral, acid or basic **soln.**) with formation of glyoxime peroxides. A survey of the formulas proposed for sym. glyoxime per-oxides leaves the true structure uncertain, though most exptl. results favor RC:N.O.O.N:CR. With asym. glyoxime peroxides, 2 formulas are necessary, viz., RC:N(:O).O.N.:CR' and RC:N.O.O.N:CR', depending upon their origin and their behavior with PCl5. It is shown, with the support of many exptl. facts, that the theory of Hantzsch and Werner is inadequate to explain the formation and the chem. behavior of these peroxides, and that the isomerism of glyoximes themselves can be explained more satisfactorily without recourse to this theory. This theory requires that every asym. dioxime should have 4 forms, viz., anti, syn and 2 amphi, and every sym. dioxime 3 forms, viz., anti, syn and amphi, and that dioximes should behave like true dioximino compds. toward all **reagents**. The investigations of P. and his collaborators (1921-1930) have shown, however, that, in many reactions, dioximes behave as if they had only one

NOH group, and that not a single one of the many sym. and asym. dioximes of 1,2-di-C:O compds. (mostly glyoximes) are known in 3 or 4 forms, and some are known in only 1 form. The chem. behavior of many dioximes is different from what would be expected according to the theory of Hantzsch and Werner, and various odd explanations have been offered by the supporters of the theory. In some cases there have been attributed to all the forms configurations derived from those of **isonitrosoketones**, but this is unsatisfactory, since it presupposes that the 2 forms of an **isonitrosoketone** are geometric isomers, which is uncertain, and that oximation of **isonitrosoketones** involves no spatial transposition of oximic OH groups, whereas in the majority of cases 2 forms of a glyoxime are obtained from NH2OH and 1 form of **isonitrosoketone**. Furthermore not all the forms of a glyoxime result directly from **isonitrosoketones**, e. g., with asym. benzil dioximes, 1 form can be prepd. only by isomerization of another form. The Hantzsch and Werner theory demands that the position of the oximic OH groups in peroxides be fixed, or else that each form of every glyoxime has a spatial configuration different from that of the other forms. Therefore the anti-forms should be incapable of dehydrogenation. The 3 forms of a sym. glyoxime should give 2 peroxides (a dioxdiazine from the syn-, a furoxan from the amphi-). The 4 forms of an asym. glyoxime should give 3 peroxides. But expts, have shown in the former case only 1 peroxide is formed, and in the latter case only 2 peroxides. To interpret all these facts, without the absurd concept that the form of a glyoxime which gives 2 peroxides can have 2 configurations and that the forms which give the same peroxide have the same configuration, it would be necessary to show that all peroxides are furoxans and that dehydrogenation of some forms involves a change in spatial position of 1 of the 2 oximic OH groups (which in asym. glyoximes is not always the same). But since the dehydrogenation of some RC(:NOH)C(:NOH)R' compds. can be accomplished at 0.degree. with a non-isomerizing **reagent**, the existence of geometric isomers must be excluded (provided that the oximic OH groups can change their spatial positions). In general this problem is an example of the impossibility of extending to compds. contg. N concepts which are applicable to those contg. no N, as also shown by Angeli in his study of the isomerism of diazo compds. Criticisms of Meisenheimer and Theilacher (C. A. 23, 3679) on the investigations of P. on dioximes are then answered. Contrary to M. and T. the compds. prepd. by Meisenhiemer, Lange and Lamparter (C. A. 19, 2819) and considered to be pure forms of p methoxybenzil dioxinie (supporting the Hantzsch and Werner theory) had incorrect m. ps. and were mixts. of the .alpha.-and .beta.-forms. Camphorquinone is not a diketone as maintained by M. and T., but is a quinone as shown by various chem. properties, particularly the behavior of its dioximes in forming only 1 peroxide, in forming no Ni complex and in their optical properties. Further confusion over the argument originates from mistranslation by M. and T. of the original Italian text. Adherence to the Hantzsch and Werner theory has led M. and T. into absurd (deductions regarding the impossibility of 1 compd. forming 2 oxidation products. These points of view are shown to be at variance with well-established exptl. fact. Dehydrogenation cannot be explained by the theory of geometric isomerism and is a reaction which is more to be expected than that of Beckmann. Therefore it is illogical to deduce the structure of compds. undergoing a Beckmann transposition by the structure of their products, and yet consider it impossible to deduce the structure of dioximes from their peroxides. The most stable form of PhC(:NOH)C(:NOH)Ph is not the syn-form supposed by M. and T., but the anti-form, which has the lowest soly., the highest m, p., forms complex Ni salts and is prepd. from the other forms by fusion or by heating with dil. AcOH. .beta.-Glyoximes are not anti-forms, for the latter do not form furoxans when boiled in 20% aq. NaOH, whereas .beta.-glyoximes react very easily under the same conditions. The reaction of .alpha.-phenylglyoxime with PhN2Cl, in which the chief product is syn-henzil dioxime, offers no evidence that .alpha.-phenylglyoxime has an amphi-form. If peroxides are

furoxans, it is possible in the anti-and syn-forms of a glyoxime for 1 of the oximic OH groups to assume the position it has in the amphi-form, and since the 4 dioximes of camphorquinone form the same furoxan, there should be in 3 of them a transposition of 1 of the 2 OH groups. Assuming (wrongly) that .beta.-and .alpha.-methylphenylglyoxime have, in agreement with M. and T., the anti-and amphi-forms, resp., and that the 2 isomeric methylphenyl peroxides are furoxans, and since the .beta.-form yields 80% of MeC:N(:O).O.N:CPh and 20% of MeC:N.O.N(:O):CPh, it follows that on dehydrogenation the greater part of the .beta.-form (anti-) should assume the configuration of the .alpha.-form (amphi-). But the .beta.-form is the stable form and it cannot isomerize to the labile .alpha.-form. Therefore it is impossible for a **reagent** with no isomerizing power (N2O4) in Et2O at 0.degree. to isomerize the .beta.-into the .alpha.-form, and therefore the theory of M. and T. of the transposition of oximic OH groups in the dehydrogenation of asym. glyoximes is absurd. Exptl. The new exptl. data represent further work in the same field and are of special importance to the present paper in that some of the results support the arguments advanced in the theoretical part. Alc. Ni(OAc)2 added to alc. H(C:NOH)3H (cf. Ber. 21, 2991(1888)) ppts. the complex Ni salt (C3H4O3N3)2Ni, orange-red, decomps. without fusion around 280.degree., also formed by heating aq. H(C:NOH)H with metallic Ni. Aq. HC(:NOH)C(:NOH)H and metallic Ni heated on a water bath form immediately a colloidal **soln**. of the complex Ni salt (C2H3O2N2)Ni, but on continued heating a brown-yellow ppt. is formed, which then decomps. with sepn. of Ni and evolution of (CN)2. Under the same conditions HC(:NOH)C(:NOH)NH2 attacks Ni immediately, which becomes covered with the orange. complex Ni salt (C2H4O23)2Ni. Aq. suspensions of .beta.-PhC(:NOH)C(:NOH)C6H4Me-p and of .beta.-PhC(:NOH)C(NOH)C6H4OMe-p, heated with Ni, form immediately the complex Ni salts (C15H13O2N2)3Ni and (C15H13O2N2)2Ni, resp., already described (cf. C. A. 18, 1400). Under the same conditions .alpha.-benzil dioxime forms the complex Ni salt (C14H11O2N2)2Ni; whereas neither the .beta.-nor .gamma.-form react with Ni. BzCl added to ice-cold MeC(:NOH)-C(:NOH)Ac in C6H5N and the product recrystd. from EtOH yields the di-Bz deriv. MeC(:NOAc)C(NOAc)Ac, m. 131.degree.. It had been impossible to obtain it with aq. NaOH as solvent (cf. C. A. 16, 2676). The formation of a di-Ac deriv., m. 71-2.degree., from PhC(:NOH)C(NOH)H described by M. and T. (C. A. 23, 3679)was confirmed. CuCl2.6H2O added to .beta.-PhC(:NOH)C(:NOH)H, each in abs. EtOH, ppts. the addn. compd. .beta.-PhC(:NOH)C(:NOH)H.CuCl2, green. .beta.-MeC(:NOH)C(:NOH)Ph (2 g.) and 10% H2SO4 (200 cc.), heated on a water bath until a colorless soin. results, cooled and the ppt. recrystd. from water, yield MeC(:NOH)Bz, m. 115.degree. (cf. Ann. 291, 292 (1896)). .beta.-MeC(:NOH)C(:NOH)Ph and 20% NaOH, heated on a water bath and the ppt. isolated by steam distn., yields methylphenylfuroxan. .beta.-MeC(:NOH)C(:NOH)Ph, agitated for some time with CuCl2.6H2O in abs. EtOH, ppts. the addn. compd. .beta.-MeC(:NOH)C(:NOH)Ph.CuCl2, dark green. Satd. aq. NaNO2 (1.5 g.) added dropwise to .beta.-MeC(:NOH)C(:NOH)Ph (2 g.) in glacial AcOH, dild. with water and made alk. with NaOII, yields 1.8 g. of a mixt. contg. 20% of 4-phenyl-5-methyl-1,2,3,6 dioxdiazinc and 80% of methylphenylfuroxan. Therefore, in acid medium the same 2 peroxides are formed as those in basic **soln**. (with NaClO) or in neutral medium (with N2O4). .beta.-MeC(:NOH)C(:NOH)C6H4OMe p and 20% NaOH and the product isolated by steam distn. yields methyl-p-methoxyphenylfuroxan, m. 65-6.degree. (cf. C. A. 23, 3665). From .beta.-MeC(:NOH)C(:NOH)C6H4OMe-P and CuCl2.6H2O, each in abs. EtOH, seps. after some time the addn. compd. .beta.-p-MeOC6H4C(:NOH)C(:NOH)Me.CuCl2, green with metallic luster. In a similar way was prepd. the addn. compd. .beta.-MeC(:NOH)C(:NOH)Bz.CuCl2, green. Prepd. by the method of Brady and Perry (C. A. 20, 752) .alpha.- and .beta.-PhC(:NOH)C(:NOH)Ph have higher m. ps. than those recorded by Beilstein (Vol. 7, 760) or by Meisenheimer and Lamparter (C. A. 18, 2153). On crystn. from AmOH rather than EtOH, the .alpha.-form m. 247-8.degree.. On crystn. from dil. EtOH contg. AcOH, and a little Ni(OAc)2 and then from dil. EtOH the .beta.-form m. 211-2.degree.. Both these m. ps. were the

same 1 yr. later. In the prepn. of the .beta.-form by the Brady and Perry method, a little diphenylfurazan was found dissolved in the excess of PhNH2. Departing from the procedure of B. and P., viz., boiling the .alpha.-form with a little PhNH2, pouring in water contg. HCl, adding dil. NaOH and recrystg. the ppt. from dil. EtOH yields 2 g. of diphenylfurazan, m. 94.degree. (cf. Ber. 21, 810(1888)). On the other hand, even on prolonged boiling of the .beta.-form with PhNH2, there is no trace of the furazan, so that the latter is the product of the dehydration of the .alpha.-form, not the .beta.-, from (cf. Ber. 21, 811(1888); Ann. 274, 34(1893)). The .beta.-form may be prepd. without any diphenylfurazan, in 100% yield, by boiling the .alpha.-form with PhNH2 (4 parts) for 5 min., pouring into dil. HCl and crystg. the product from dil. EtOH contg. a little AcOH and Ni(OAc)2. The .alpha.-form (1 g.), fused, cooled immediately and treated with EtOH leaves 0.1 g. of undissolved substance which is filtered, a little dil. AcOH and Ni(OAc)3 added to the filtrate, dild, with water and the ppt. agitated with dil. NaOH, leaves 0.1 g. of diphenylfurazan, while the .beta.-form passes into **soln.** and reppts. with dil. H2SO4. According to M. and T. (loc. cit.) the yield of the .beta.-form would be 50% with no furazan, which proves that the reaction does not always proceed in just the same way and is not a simple isomerization limited by the inverse reaction. .gamma.-Benzil dioxime (1 g.) heated to 170.degree. and treated with EtOH leaves a residue of 0.15 g. of the .alpha.-form. A little dil. AcOH and Ni(OAc)2 added to the filtrate, and dild. with water, ppts. 0.7 g. of the. .beta.-form. This is more .alpha.-compd. than obtained by Beckmann and Koster (Ann. 274, 25(1893)) or by Auwers and Meyer (Ber. 22, 712(1888)). Dil. alc. .gamma.-benzil dioxime and a little dil. AcOH and Ni(OAc)2, heated on a boiling water bath, ppts. (C14H11O2N2)2Ni (the .alpha.-complex), while the **soln**, contains .beta.-benzil dioxime, which seps. on cooling. The yield of .alpha.-compd. varies from 40 to 70%, and it does not originate from the .beta.-form, for isomerization of the latter in dil. AcOH is extremely slow. The .gamma.-form and aq. NaOH heated on a water bath isomerizes to the .beta. -form (cf. Ber. 22, 713(1889)) and the .beta.-form also results from heating the .gamma.-form with concd. HCl in a closed tube at 100.degree.. Early expts. on the. prepn. of diphenylglyoxime peroxide by NaClO were limited to .beta.-benzil dioxime (cf. Gazz. chim. ital. 36, ii, 103(1906)). Applying this method to the .alpha.-and .gamma.-forms, the product from the .alpha.-form is yellow and difficult to decolorize, whereas that from the .gamma.-form, after recrystn. from EtOH and from ligroin, m. 116-7.degree.. Not being able to exclude a priori the possibility of extranuclear O in diarylfuroxans having an influence on the nitration of the aryl groups, expts. were carried out to ascertain whether the behavior of the dehydrogenation products with HNO3 would indicate which of the structures: ArC:N.O.N(:O):CAr, ArC:N.O.O.N:CAr or ArC:CAr.N.O.N.O, (Green and Rowe) is the true one. The results do not settle the question. Both diphenylglyoxime peroxide and diphenylfurazan form with cold HNO3 (d. 1.45) the resp. di-p-nitro deriv., which indicates that if the furazan is sym. the peroxide should also be so. On the contrary, by warming with HNO3 (d. 1.40), the diphenyl peroxide forms the p-nitro deriv. and the di-p-methoxyphenyl peroxide the dinitro deriv., whereas diphenylfurazan does not react. The diphenyl peroxide boiled for some time in HNO3 (d. 1.40) and the product recrystd. from EtOH yields p-nitrodiphenylglyoxime peroxide, Ph(C2N2O2)C6H4NO2.p, straw color, m. 114-50.degree., sol. in concd. H2SO4, transformed by cold HNO3, (d. 1.45) into di-p-nitrodiphenylglyoxime peroxide, which, recrystd. from EtOH. m. 197-8.degree., and from glacial AcOH, m, 203-4.degree.; also formed directly from the diphenyl peroxide in cold HNO3 (d. 1.45). These **syntheses** in conjunction with the expts. of Werner (Ber. 27, 2848(1894)) establish the positions of the NO2 groups in both compds. Di-p-methoxyphenylglyoxime peroxide warmed with HNO3 (d. 1.40), cooled and the ppt. recrystd. from EtOH, yields dinitro-di-p-methoxyphenylglyoxime peroxide, (C2N2O2) [C6H3(NO2)OMe]2, yellowish, m. 180-1.degree..

According to Meisenheimer, Lange and Lamparter (C. A. 19, 2819), there are .alpha.-, .beta.-, .gamma.- and .delta.-forms of p-methoxybenzil dioxime. .alpha.-Form. The method of M., L. and L. leads to a mixt. of .alpha. and .beta. forms, but the pure .alpha. form may be prepd. in another way. The product of the reaction of NH2OH with .alpha.1- and .alpha.2-p-MeOC5H4COC(:NOH)Ph (cf. M., L. and L., loc. cit.) is dissolved in EtOH, heated with a little dil. AcOH and Ni-(OAc)2, filtered, washed with EtOH, the residue decompd. with concd. HCl in Et2O and the insol, product recrystd. from AmOH, which yields the pure .alpha.-form, m. 223-4.degree.. A sample after 8 yr. m. 217-9.degree.. .beta.-Form. Prepd. by the method of Mp, L. and L., this m. 176.degree. and contains unaltered .alpha.-compd. To eliminate the latter, the product is crystd. from dil. EtOH contg. a little AcOH and Ni(OAc)2, filtered to remove the Ni complex of the .alpha.-form and the residue recrystd. from dil. EtOH, which gives a product which m. 185.degree. (no change after 1 yr.). It is prepd. much more easily by boiling for a few min. the .alpha.-form (5 g.) with PhNH2 (20 cc.), pouring into dil. HCl and proceeding as before. The properties of the di-Ac deriv. agree with those described by M., L, and L. The di-Bz deriv., p-MeOC6H4C(:NOBz)C(:NOBz)Ph, prepd. from the .beta.-form in NaOH and BzCl, with crystn. from EtOH, m. 129-30.degree., can be hydrolyzed. The .beta.-form when fused or when its dil. alc. **soln.** is heated with dil. AcOH and Ni(OAc)2, undergoes isomerization to the .alpha.-form. The 1st method gives a low yield, while the 2nd method is slow but yields a very pure product. The .beta.-form in 10% NaOH and 10% NaClO ppts. immediately 100% of a peroxide, which, recrystd. from EtOH, m. 106-7.degree., the m. p. found by M., L. and L. (loc. cit.) for the peroxide prepd. from the .gamma.-form. Recrystd. from AcMe, it m. 108-9.degree.. From the alc. mother liquor can be isolated by fractional crystn. an isomeric peroxide, m. 102-3.degree.. These results agree well with those of Kinney (C. A. 23, 2971). These 2 peroxides are designated .alpha.- and .beta.-peroxides to distinguish them from the furoxans and dioxdiazines which have been described in the theoretical part (loc. cit.). .gamma.-Form.

The peroxide prepd. by M., L. and L. from NH2OH.HCl and .beta.1-p-MeOC6H4COC(:NOH)Ph, with subsequent oxidation by NaClO, when fractionally recrystd. yields the .alpha.-peroxide and a small proportion of .beta.-peroxide, which shows that the so-called .gamma.-p-methoxybenzil dioxime of M., L. and L. contains a little of the .beta.-form. M., L. and L. found that the solid .gamma.-form isomerizes slowly into the .beta.-form, and in EtOH or Et2O isomerizes rapidly, but expts. by P. show that some .alpha.-compd. is also formed. That the .alpha.-form originates directly from the .beta.-form (not through. the .gamma.-form) is proved by the fact that when the substance which m. 89-91.degree. is heated in dil. EtOH with a little AcOH and Ni(OAc)2 there seps. the Ni complex of the .alpha.-form, which, eliminated by filtration, yields a mother liquor contg. the .beta.-form. The latter then isomerizes slowly to the .alpha.-form. .delta.-Form. Expts. by Kinney (loc. cit.) have proved that the substance supposed by M., L. and L. to be .beta.-phenylanisylfuroxan is a mixt. of 2 methyl-p-methoxyphenylglyoxime peroxides. It is impossible at present to identify the forms in this mixt. because the 2 peroxides originate from the .alpha.- as well as from the .gamma.-dioxime. It is certain that 3 p-methoxybenzil dioximes exist, of which the .alpha.- and .beta.-forms have been obtained pure, with m. ps. of 223.degree. and 185.degree., resp., while the .gamma.-form m. 89-91.degree. in its so far unpurified state (contg. some of the .beta.-form). The mixt. of 2 peroxides of M., L. and L. which m. 95-7.degree. (loc. cit.) when mixed with the .alpha.-peroxide (m. 108-9.degree.) m. 97-105.degree., and this is in accordance with the results of Milone (cf. C. A. 24, 1633) on the equil. between the isomeric peroxides obtained by dehydrogenating .beta.-MeC(:NOH)C(:NOH)Ph and .beta.-p-MeOC4H4C(NOH)C(:NOH)Me.

L20 ANSWER 16 OF 16 HCAPLUS COPYRIGHT 2003 ACS

ACCESSION NUMBER: 1923:17211 HCAPLUS
DOCUMENT NUMBER: 17:17211
ORIGINAL REFERENCE NO.: 17:2711i,2712a-f
TITLE: New syntheses in the imidazole group
AUTHOR(S): Sarasin, Jean
SOURCE: Helvetica Chim. Acta. (1923), 6, 377-85
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB S. desired to **synthesize** histamine, pilocarpinee and their homologs and endeavored to obtain 4- or 5-allyl derivs. of imidazole (I). 1-Methyl-4-chloroimidazole (II) with C3H5Cl in Et2O or petr. ether and Na yielded 1-methylimidazole, b. 195-6.degree., and also diallyl by reduction. Further work showed that II does not yield its Cl easily, failing to interact with Grignard **reagents**, NaHC(CO2Et)2, Et2NH or KI up to 150.degree.. When heated to 140.degree. with 40% CH2O in tubes for 4 hrs., II gave 1-methyl-2-methylol-4-chloroimidazole, m. 109-10.degree.. When warmed at 160-70.degree. for several hrs. with red P and HI it yielded after distn. in vacuo and treatment with K2CO3 1,2-dimethylimidazole (Jowett and Potter, J. Chem. Soc. 83, 469(1903)), b. 205-6.degree.. The picrate m. 179-80.degree.. AcCH(CO2Et).C3H5 was dissolved in cold KOH and after 24 hrs. NaNO2 was added by drops to the iced mixt. The **isonitrosoacetone** formed was purified by **soln.** in NaOH, the **soln.** being extd. by Et2O. The **isonitrosoalyllacetone** formed m. 46.degree.. It was treated in glacial AcOH with Sn and HCl for 36 min. at 50.degree. and the product was then treated with H2S. Aminoallylacetone-HCl (III), m. 152-3.degree. (decompn.). 4(5)-Methyl-5(4)-allyl-2-mercaptoimidazole (IV), m. 238-9.degree., was prepd. according to the method of Gabriel and Pinkus (Ber. 26, 2203(1893)) by warming III with a concd. NH4SCN. IV crystd. slowly meanwhile. This suspended in aq. FeCl3 was warmed 0.5 hr. on the H2O bath, K2CO3 was then added and FeCO3 which sepd. was filtered. The acidified filtrate was evapd. to dryness. 4(5)-Methyl-5(4)-allylimidazole (V), b12 180-1.degree., m. 71.degree.. The oxidation of IV with other oxidizing agents. as K2S2O8 and H2O3 gave low yields. MeI and V were heated for 0.5 hr. on the H2O bath. 1,4-Dimethyl-5-allylimidazole and 1,5-dimethyl-4-allylimidazole were liberated by K2CO3, the mixt. b12 125-8.degree.. The HBr salt of V was warmed 5 hrs. at 90-100.degree. with 25% HBr, the mixt. was evapd. to dryness and the cryst. residue was dissolved in H2O made alk. with K2CO3. 4(5)-Methyl-5(4)-.beta.-bromopropylimidazole (VI) m. 109-10.degree.. VI in concd. NH4OH after standing 24 hrs. was warmed on the bath and then evapd. in vacuo. The residue was taken up again in K2CO3 **soln.** and CHCl3 which dissolved the 4(5)-methyl-5(4)-.beta.-aminopropylimidazole, b10 185-6.degree., b2 148-9.degree.. The dihydrochloride is hygroscopic and m. 217.degree.. The dipicrate, m. 229-30.degree.. VI when warmed with dry Et2NH in abs. alc. gave a mass which with K2CO3 gave 4(5)-methyl-5(4)-diethylaminopropylimidazole, b2 143-4.degree.. The dihydrochloride, m. 199-200.degree.. The dipicrate. m. 178-9.degree.. A suspension of V in CS2 was treated with Br in CS2. The Br disappeared at once, the HBr salt was filtered, washed with CS2, dried in vacuo and treated in H2O with K2CO3 giving 4(5)-methyl-5(4)-.beta.,.gamma.-dibromopropylimidazole, m. 116-7.degree.. 4(5)-Methyl-5(4)-.beta.,-.gamma.-chloroiodopropylimidazole, m. 94-5.degree., was prepd. in a similar manner.

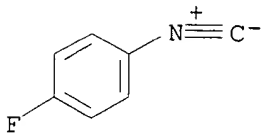
=>
=>

=> select hit rn l20 1-16
E1 THROUGH E9 ASSIGNED

=> fil reg

```
FILE 'REGISTRY' ENTERED AT 11:53:17 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file
provided by InfoChem.

STRUCTURE FILE UPDATES:   12 MAR 2003  HIGHEST RN 498527-50-7
DICTIONARY FILE UPDATES:  12 MAR 2003  HIGHEST RN 498527-50-7

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

  Please note that search-term pricing does apply when
  conducting SmartSELECT searches.

Crossover limits have been increased.  See HELP CROSSOVER for details.

Experimental and calculated property data are now available.  See HELP
PROPERTIES for more information.  See STNote 27, Searching Properties
in the CAS Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=>
=>

=> s e1-e9
             1 10340-91-7/BI
               (10340-91-7/RN)
             1 10349-38-9/BI
               (10349-38-9/RN)
             1 24075-34-1/BI
               (24075-34-1/RN)
             1 2769-71-3/BI
               (2769-71-3/RN)
             1 598-45-8/BI
               (598-45-8/RN)
             1 7175-47-5/BI
               (7175-47-5/RN)
             1 7188-38-7/BI
               (7188-38-7/RN)
             1 931-53-3/BI
               (931-53-3/RN)
             1 931-54-4/BI
               (931-54-4/RN)
L21          9 (10340-91-7/BI OR 10349-38-9/BI OR 24075-34-1/BI OR 2769-71-3/BI
               OR 598-45-8/BI OR 7175-47-5/BI OR 7188-38-7/BI OR 931-53-3/BI
              OR 931-54-4/BI)

=>
=>

=> d ide can l21 1-9

L21  ANSWER 1 OF 9  REGISTRY  COPYRIGHT 2003 ACS
RN   24075-34-1  REGISTRY
CN   Benzene, 1-fluoro-4-isocyano- (9CI)  (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN   Phenyl isocyanide, p-fluoro- (8CI)
OTHER NAMES:
CN   4-Fluorophenyl isonitrile
CN   p-Fluorophenyl isocyanide
FS   3D CONCORD
```

MF C7 H4 F N
LC STN Files: BEILSTEIN*, CA, CAPLUS, CASREACT, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)



21 REFERENCES IN FILE CA (1962 TO DATE)
21 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1: 137:311068

REFERENCE 2: 137:263220

REFERENCE 3: 135:61470

REFERENCE 4: 134:367073

REFERENCE 5: 134:266468

REFERENCE 6: 134:65447

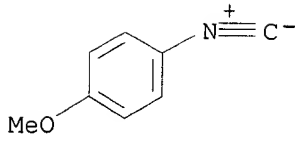
REFERENCE 7: 133:350379

REFERENCE 8: 131:271682

REFERENCE 9: 130:125257

REFERENCE 10: 128:321803

L21 ANSWER 2 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **10349-38-9** REGISTRY
CN Benzene, 1-isocyano-4-methoxy- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Phenyl isocyanide, p-methoxy- (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1-Isocyano-4-methoxybenzene
CN 4-Methoxy-1-isocyanobenzene
CN 4-Methoxyphenyl isocyanide
CN 4-Methoxyphenyl isonitrile
CN Anisyl isonitrile
CN p-Anisyl isocyanide
CN p-Anisyl isonitrile
CN p-Methoxyphenyl isocyanide
CN p-Methoxyphenyl isonitrile
FS 3D CONCORD
MF C8 H7 N O
CI COM
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, GMELIN*, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)



137 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
137 REFERENCES IN FILE CAPLUS (1962 TO DATE)
10 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 137:352859

REFERENCE 2: 137:325546

REFERENCE 3: 137:263135

REFERENCE 4: 137:262607

REFERENCE 5: 135:344262

REFERENCE 6: 135:137537

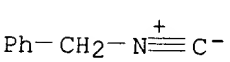
REFERENCE 7: 135:61470

REFERENCE 8: 134:367073

REFERENCE 9: 134:266468

REFERENCE 10: 134:65447

L21 ANSWER 3 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **10340-91-7** REGISTRY
CN Benzene, (isocyanomethyl)- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN (Isocyanomethyl)benzene
CN Benzyl isonitrile
FS 3D CONCORD
MF C8 H7 N
CI COM
LC STN Files: AGRICOLA, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, DETHERM*, GMELIN*, HODOC*, IFICDB, IFIPAT, IFIUDB, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



355 REFERENCES IN FILE CA (1962 TO DATE)
6 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
356 REFERENCES IN FILE CAPLUS (1962 TO DATE)
13 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:137405

REFERENCE 2: 138:107001

REFERENCE 3: 138:75102

REFERENCE 4: 138:65539

REFERENCE 5: 138:39391

REFERENCE 6: 138:10882

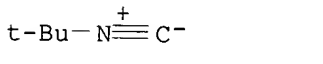
REFERENCE 7: 137:352988

REFERENCE 8: 137:337453

REFERENCE 9: 137:295253

REFERENCE 10: 137:267993

L21 ANSWER 4 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **7188-38-7** REGISTRY
CN Propane, 2-isocyano-2-methyl- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN tert-Butyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1,1-Dimethylethyl isocyanide
CN 2-Isocyano-2-methylpropane
CN t-Butylisocyanide
CN t-Butylisonitrile
CN tert-Butyl isonitrile
AR 17053-83-7
FS 3D CONCORD
DR 17053-83-7
MF C5 H9 N
CI COM
LC STN Files: AGRICOLA, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CEN, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, CSNB, GMELIN*, HODOC*, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, NIOSHTIC, PROMT, RTECS*, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



1619 REFERENCES IN FILE CA (1962 TO DATE)
25 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1621 REFERENCES IN FILE CAPLUS (1962 TO DATE)
17 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:153646

REFERENCE 2: 138:137590

REFERENCE 3: 138:137572

REFERENCE 4: 138:136843

REFERENCE 5: 138:136777

REFERENCE 6: 138:116831

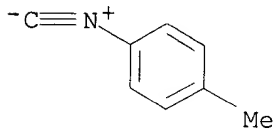
REFERENCE 7: 138:107001

REFERENCE 8: 138:106817

REFERENCE 9: 138:106809

REFERENCE 10: 138:89899

L21 ANSWER 5 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **7175-47-5** REGISTRY
CN Benzene, 1-isocyano-4-methyl- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN p-Tolyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1-Isocyano-p-toluene
CN 4-Methylphenyl isocyanide
CN 4-Methylphenyl isonitrile
CN 4-Tolyl isocyanide
CN p-Methylphenyl isocyanide
CN p-Tolyl isonitrile
FS 3D CONCORD
DR 128202-86-8
MF C8 H7 N
CI COM
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMINFORMRX, GMELIN*, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)



209 REFERENCES IN FILE CA (1962 TO DATE)
3 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
210 REFERENCES IN FILE CAPLUS (1962 TO DATE)
15 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:146644

REFERENCE 2: 137:325546

REFERENCE 3: 137:263220

REFERENCE 4: 137:56455

REFERENCE 5: 136:37753

REFERENCE 6: 135:195695

REFERENCE 7: 135:137537

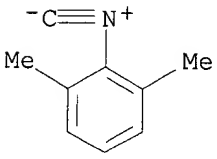
REFERENCE 8: 134:367073

REFERENCE 9: 134:366844

REFERENCE 10: 134:266468

L21 ANSWER 6 OF 9 REGISTRY COPYRIGHT 2003 ACS

RN **2769-71-3** REGISTRY
CN Benzene, 2-isocyano-1,3-dimethyl- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN 2,6-Xylyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1-Isocyano-2,6-dimethylbenzene
CN 2,6-Dimethylisocyanobenzene
CN 2,6-Dimethylphenyl isocyanide
CN 2,6-Dimethylphenylisonitrile
CN 2,6-Xylene isonitrile
CN 2,6-Xylyl isonitrile
CN 2-Isocyano-1,3-dimethylbenzene
CN 2-m-Xylyl isocyanide
FS 3D CONCORD
DR 182361-64-4
MF C9 H9 N
CI COM
LC STN Files: BEILSTEIN*, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN*, IFICDB, IFIPAT, IFIUDB, MEDLINE, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



601 REFERENCES IN FILE CA (1962 TO DATE)
5 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
603 REFERENCES IN FILE CAPLUS (1962 TO DATE)
4 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:122845

REFERENCE 2: 138:106781

REFERENCE 3: 138:106755

REFERENCE 4: 138:82441

REFERENCE 5: 138:65554

REFERENCE 6: 138:65539

REFERENCE 7: 138:47038

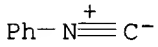
REFERENCE 8: 138:38829

REFERENCE 9: 138:10880

REFERENCE 10: 137:384963

L21 ANSWER 7 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **931-54-4** REGISTRY
CN Benzene, isocyano- (9CI) (CA INDEX NAME)

OTHER CA INDEX NAMES:
CN Phenyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN Benzoisonitrile
CN Isocyanobenzene
CN Phenyl isonitrile
FS 3D CONCORD
DR 128202-85-7
MF C7 H5 N
CI COM
LC STN Files: BEILSTEIN*, BIOSIS, BIOTECHNO, CA, CAOLD, CAPLUS, CASREACT, CEN, CHEMINFORMRX, CHEMLIST, DETHERM*, EMBASE, GMELIN*, IFICDB, IFIPAT, IFIUDB, MEDLINE, NIOSHTIC, SPECINFO, TOXCENTER, USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



443 REFERENCES IN FILE CA (1962 TO DATE)
12 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
443 REFERENCES IN FILE CAPLUS (1962 TO DATE)
35 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:106814

REFERENCE 2: 137:325314

REFERENCE 3: 137:263220

REFERENCE 4: 137:263163

REFERENCE 5: 137:262607

REFERENCE 6: 137:131360

REFERENCE 7: 137:109234

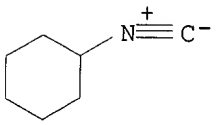
REFERENCE 8: 137:100448

REFERENCE 9: 137:47345

REFERENCE 10: 137:24099

L21 ANSWER 8 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **931-53-3** REGISTRY
CN Cyclohexane, isocyano- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Cyclohexyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN Cyclohexaneisonitrile
CN Cyclohexyl isonitrile
CN Isocyanocyclohexane
FS 3D CONCORD
MF C7 H11 N
CI COM
LC STN Files: AGRICOLA, AQUIRE, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN*, IFICDB, IFIPAT, IFIUDB, MSDS-OHS, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)

Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



740 REFERENCES IN FILE CA (1962 TO DATE)
10 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
744 REFERENCES IN FILE CAPLUS (1962 TO DATE)
30 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:142315

REFERENCE 2: 138:107001

REFERENCE 3: 138:106814

REFERENCE 4: 138:89520

REFERENCE 5: 138:73351

REFERENCE 6: 138:65539

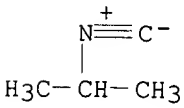
REFERENCE 7: 138:39044

REFERENCE 8: 138:38829

REFERENCE 9: 137:384790

REFERENCE 10: 137:353129

L21 ANSWER 9 OF 9 REGISTRY COPYRIGHT 2003 ACS
RN **598-45-8** REGISTRY
CN Propane, 2-isocyano- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Isopropyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN 2-Isocyanopropane
CN Isopropyl isonitrile
FS 3D CONCORD
MF C4 H7 N
CI COM
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CSCHEM, GMELIN*, HODOC*, IFICDB, IFIPAT, IFIUDB, MEDLINE, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)



150 REFERENCES IN FILE CA (1962 TO DATE)
4 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
150 REFERENCES IN FILE CAPLUS (1962 TO DATE)
8 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:107001

REFERENCE 2: 138:75102

REFERENCE 3: 136:200252

REFERENCE 4: 136:167498

REFERENCE 5: 136:69909

REFERENCE 6: 135:344419

REFERENCE 7: 135:331409

REFERENCE 8: 135:269156

REFERENCE 9: 134:340448

REFERENCE 10: 134:50577

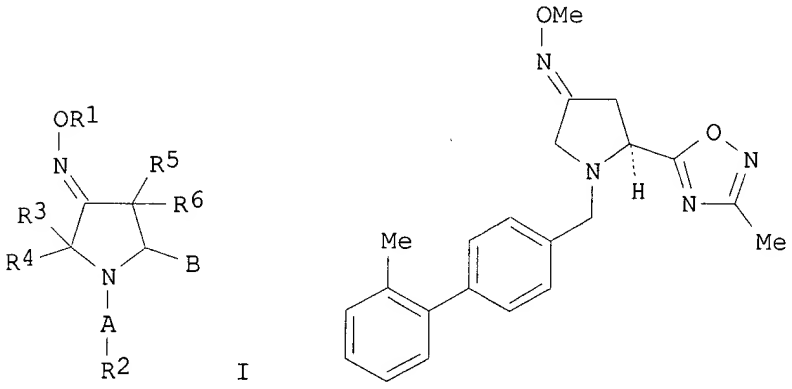
```
=> fil hcaplus
FILE 'HCAPLUS' ENTERED AT 11:53:50 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is
held by the publishers listed in the PUBLISHER (PB) field (available
for records published or updated in Chemical Abstracts after December
26, 1996), unless otherwise indicated in the original publications.
The CA Lexicon is the copyrighted intellectual property of the
the American Chemical Society and is provided to assist you in searching
databases on STN.  Any dissemination, distribution, copying, or storing
of this information, without the prior written consent of CAS, is
strictly prohibited.

FILE COVERS 1907 - 13 Mar 2003  VOL 138 ISS 11
FILE LAST UPDATED: 12 Mar 2003  (20030312/ED)

 This file contains CAS Registry Numbers for easy and accurate
 substance identification.


=>
=>

=> d stat que l23 nos
L1              STR
L5         1338 SEA FILE=REGISTRY SSS FUL L1
L8              STR
L9           36 SEA FILE=REGISTRY SUB=L5 SSS FUL L8
L10          37 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L9
L12         464 SEA FILE=REGISTRY ABB=ON  PLU=ON  ISONITR?
L13       17185 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L12 OR ?ISONITR?
L14         306 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)REAGENT
L17        1686 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)(SOLUTION OR SOLID(W)PHA
                SE)
L18      126770 SEA FILE=HCAPLUS ABB=ON  PLU=ON  SYNTHE?(L)(SOLUTION OR
                SOLID(W)PHASE)
L19          17 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L14 AND L17 AND L18
L20          16 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L19 NOT L10
L22          10 SEA FILE=HCAPLUS ABB=ON  PLU=ON  ("PAGE PATRICK"/AU OR "PAGE
                PATRICK"/IN OR "PAGE PATRICK E"/AU)
L23           9 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L22 NOT (L10 OR L20)


=>
=>

=> d ibib abs hitrn l23 1-9

L23  ANSWER 1 OF 9  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:         2002:977813  HCAPLUS
DOCUMENT NUMBER:          138:55968
TITLE:                    Preparation of (biphenylylcarbonyl)(oxadiazolyl or
                          thiadiazolyl)pyrrolidinone oximes as oxytocin receptor
                          antagonists for treatment of preterm labor, premature
                          birth, and dysmenorrhea
INVENTOR(S):              Schwarz, Matthias; Page, Patrick; Pomel,
                          Vincent; Quattropani, Anna; Thomas, Russell J.
PATENT ASSIGNEE(S):       Applied Research Systems ARS Holding N.V., Neth.
```

Antilles
SOURCE: PCT Int. Appl., 152 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002102799	A2	20021227	WO 2002-EP6629	20020614

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

PRIORITY APPLN. INFO.: EP 2001-113632 A 20010618
OTHER SOURCE(S): MARPAT 138:55968
GI



AB The present invention is related the prepn. and use of title compds. I [wherein A = CO, CO2, SO2, SO2NH, or CH2; B = oxadiazole or thiadiazole ring; R1 = alkyl, alkenyl, alkynyl, (hetero)aryl, or alkyl(hetero)aryl; or OR1 = heterocyclic ring optionally fused with a (hetero)aryl or cycloalkyl ring; R2 = (cyclo)alkyl, alkenyl, alkynyl, (alkyl)aryl, (alkyl)heteroaryl, heteroarylalkyl, acyl, etc.; R3-R6 = independently H, halo, alkyl, or alkoxy; or geometrical isomers, enantiomers, diastereomers, racemates, or pharmaceutically acceptable salts thereof], as well as pharmaceutical formulations contg. I, as oxytocin receptor antagonists. For example, (2S,4EZ)-1-(tert-butoxycarbonyl)-4-(methoxyimino)-2-pyrrolidinecarboxylic acid and acetamidoxime (prepn. of reactants given) in DCM were stirred overnight at room temp. to give the oxadiazole intermediate (60%). N-deprotection using HCl gas, followed by addn. of 2'-methyl[1,1'-biphenyl]-4-carboxylic acid and DMAP and sepn. of the (E)- and (Z)-isomers by column chromatog. afforded (3E,5S)- and (3Z,5S)-II in 34% and 33% yield, resp. The latter displayed binding affinity for the human oxytocin receptor (hOT-R) in vitro with IC50 of 0.009 .mu.M, inhibited oxytocin-induced Ca2+ mobilization mediated by hOT-R in vitro with IC50 of

0.004 .mu.M, and reduced oxytocin-induced uterine contractions in non-pregnant female rats by 74.4% .+-. 4.2% at doses of 30 mg/kg p.o. I are useful in the treatment and/or prevention of disease states mediated by oxytocin, including preterm labor, premature birth, and dysmenorrhea.

L23 ANSWER 2 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:733957 HCAPLUS
DOCUMENT NUMBER: 132:104575
TITLE: Origin of the slow-binding inhibition of aldolase by D-glycero-tetrulose 1-phosphate (D-erythrulose 1-phosphate) from the comparison with the isosteric phosphonate analog
AUTHOR(S): **Page, Patrick**; Blonski, Casimir; Perie, Jacques
CORPORATE SOURCE: Groupe Chimie Organique Biologique, Univ. Paul Sabatier, Toulouse, F-31062, Fr.
SOURCE: European Journal of Organic Chemistry (1999), (11), 2853-2857
CODEN: EJOCFK; ISSN: 1434-193X
PUBLISHER: Wiley-VCH Verlag GmbH
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The mechanistic reaction pathway for the slow-binding inhibition of rabbit muscle aldolase (I) by D-glycero-tetrulose 1-phosphate (D-erythrulose 1-phosphate) (II) was investigated through the use of its phosphonomethyl isostere (III) which was synthesized for this study. III was not a substrate nor a slow-binding inhibitor, but interfered in the I-catalyzed reaction with the substrate, fructose 1,6-diphosphate, in a competitive manner. It was found that phosphonate III formed an iminium ion with I and underwent subsequent .alpha.-proton abstraction to form an enamine intermediate. It was shown from these results that I slow-binding inhibition by II was consistent with a phosphate .beta.-elimination reaction through the enamine intermediate. This mechanism takes into account the stereochem. features known for I, the parallel between enzyme activity recovery and phosphate release after action of II, and also the same reaction from dihydroxyacetone phosphate.
REFERENCE COUNT: 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 3 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:485969 HCAPLUS
DOCUMENT NUMBER: 131:199902
TITLE: Synthesis of phosphono analogues of dihydroxyacetone phosphate and glyceraldehyde 3-phosphate
AUTHOR(S): **Page, Patrick**; Blonski, Casimir; Perie, Jacques
CORPORATE SOURCE: Groupe de Chimie Organique Biologique, UMR 5623, Universite Paul Sabatier, Toulouse, 31062, Fr.
SOURCE: Bioorganic & Medicinal Chemistry (1999), 7(7), 1403-1412
CODEN: BMECEP; ISSN: 0968-0896
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The present paper describes the synthetic routes of six phosphono analogs of dihydroxyacetone phosphate and five phosphono analogs of glyceraldehyde 3-phosphate through .alpha.-, .beta.- and .gamma.-hydroxyphosphonate esters precursors contg. a protected carbonyl group. In some situations, depending on the sequence used for the deprotection of the phosphonate and carbonyl groups, the aldol/ketol rearrangement allowed the synthesis of either dihydroxyacetone phosphate or glyceraldehyde 3-phosphate analogs from the same precursors. All these analogs are of interest both as active-site probes and as potential substrates for glycolytic enzymes such

as fructose 1,6-diphosphate aldolases (EC 4.1.2.13).
REFERENCE COUNT: 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

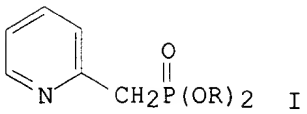
L23 ANSWER 4 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:35812 HCAPLUS
DOCUMENT NUMBER: 130:153966
TITLE: Solid-phase synthesis of tyrosine peptide aldehydes. Analogs of (S)-MAPI
AUTHOR(S): **Page, Patrick**; Bradley, Mark; Walters, Iain; Teague, Simon
CORPORATE SOURCE: Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK
SOURCE: Journal of Organic Chemistry (1999), 64(3), 794-799
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 130:153966
AB We report an efficient solid-phase synthesis of C-terminal tyrosine peptide aldehydes based on the HIV protease inhibitors (S)-MAPI and GE 20372 A. Our strategy consisted of anchoring the side chain of Dde-Tyrosinol onto the brominated Wang linker deriv. ((4-bromomethyl)-phenoxy-allyl acetate) to give after ester hydrolysis the N.alpha.-(Dde)-O-(4-methylphenoxyacetic acid)-L-Tyrosinol template. This was attached to aminomethyl resin and elongated using std. Fmoc protocols. Importantly there was no evidence of esterification side reactions. The unsym. substituted urea linkage of the (S)-MAPI family was incorporated using the N.alpha.-(4-nitrophenyloxycarbonyl)amino acid tert-Bu esters following which the protected tetrapeptide alc. immobilized on the solid support was oxidized to its corresponding aldehyde using sulfur trioxide-pyridine. The efficiency and reliability of the oxidn. step was dramatically improved by the incorporation of a small PEG-spacer between the linker and the solid support. The tetrapeptides were cleaved by acidolysis, purified by RP HPLC, and isolated in high yield and purity, demonstrating the success of the whole synthetic process.
REFERENCE COUNT: 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 5 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1998:482708 HCAPLUS
DOCUMENT NUMBER: 129:244972
TITLE: The synthesis of symmetrical spermine conjugates using solid-phase chemistry
AUTHOR(S): **Page, Patrick**; Burrage, Sarah; Baldock, Lorraine; Bradley, Mark
CORPORATE SOURCE: Department of Chemistry, University of Southampton, SO17 1BJ, UK
SOURCE: Bioorganic & Medicinal Chemistry Letters (1998), 8(13), 1751-1756
CODEN: BMCLE8; ISSN: 0960-894X
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The utility of spermine, selectively functionalized and immobilized on a solid support by means of the Wang "oxycarbonyl" linker is demonstrated by the solid-phase synthesis of a no. of spermine conjugates including the natural product and potent antihypertensive agent kukoamine. The synthesis opens up the area of solid-phase spermine chem. and library generation based on the sym. spermine scaffold.
REFERENCE COUNT: 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 6 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1998:466836 HCAPLUS
DOCUMENT NUMBER: 129:213352
TITLE: Interaction of phosphonomethyl analog of dihydroxyacetone phosphate with rabbit muscle aldolase
AUTHOR(S): **Page, Patrick**; Blonski, Casimir; Perie, Jacques
CORPORATE SOURCE: Bat. II R1, UMR CNRS 5623, Groupe de Chimie Organique Biologique, Universite Paul Sabatier, Toulouse, 31062, Fr.
SOURCE: Biochimica et Biophysica Acta (1998), 1386(1), 59-64
CODEN: BBACAQ; ISSN: 0006-3002
PUBLISHER: Elsevier Science B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Aldolase presents the same binding affinity for dihydroxyacetone phosphate and its phosphonomethyl analog, but the partition coeff. between the intermediates from the Michaelis complex to the eneamine is different. The effects of the structural modification of the triose phosphate substrate on the interaction with rabbit muscle aldolase are discussed in connection with the mechanistic pathway and the three-dimensional structure of the enzyme.
REFERENCE COUNT: 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 7 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1996:84271 HCAPLUS
DOCUMENT NUMBER: 124:261471
TITLE: An improved chemical and enzymic synthesis of new fructose derivatives for import studies by the glucose transporter in parasites
AUTHOR(S): **Page, Patrick**; Blonski, Casimir; Perie, Jacques
CORPORATE SOURCE: CNRS, Univ. Paul Sabatier, Toulouse, 31062, Fr.
SOURCE: Tetrahedron (1996), 52(5), 1557-72
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier
DOCUMENT TYPE: Journal
LANGUAGE: English
AB This paper presents the chemoenzymic synthesis of D-fructose analogs substituted at position C6. These compds. are the unique products of rabbit muscle aldolase catalyzed aldolization of D-glyceraldehyde analogs (obtained by stereospecific chem. synthesis) with DHAP, followed by a dephosphorylation step with acid phosphatase.

L23 ANSWER 8 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1993:81025 HCAPLUS
DOCUMENT NUMBER: 118:81025
TITLE: Simple and convenient synthesis of 2-phosphonomethylpyridines
AUTHOR(S): **Page, Patrick**; Mazieres, Marie Rose; Bellan, Jacques; Sanchez, Michel; Chaudret, Bruno
CORPORATE SOURCE: Lab. Synth., Struct. React. Mol. Phosphorees, Univ. Paul Sabatier, Toulouse, 31062, Fr.
SOURCE: Phosphorus, Sulfur and Silicon and the Related Elements (1992), 70(3-4), 205-10
CODEN: PSSLEC; ISSN: 1042-6507
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 118:81025
GI



I

AB The Michaelis-Becker-Nylen reaction is well suited for the synthesis of 2-phosphonomethylpyridines. This four steps method has been improved in a one pot reaction beginning from starting materials 2-(chloromethyl)pyridine and phosphonate anion, (RO)2P(O)H [prepd. from (Me2N)2P(O)H and ROH (e.g., R = Et, p-MeC6H4)] using com. reagents. By this general procedure seven new 2-phosphonomethylpyridines I were prepd. under mild conditions with higher yields.

L23 ANSWER 9 OF 9 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1970:498046 HCAPLUS
DOCUMENT NUMBER: 73:98046
TITLE: Pineapple growth and nutrition over a plant crop cycle in southeastern Queensland. 2. Uptake and concentrations of nitrogen, phosphorus, and potassium
AUTHOR(S): Black, Roger Foster; **Page, Patrick E.**
CORPORATE SOURCE: Hort. Res. Sta., Queensland Dep. Primary Ind., Nambour, Australia
SOURCE: Queensland Journal of Agricultural and Animal Sciences (1969), 26(3), 385-405
CODEN: QJAAA3; ISSN: 0033-6173
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Cayenne pineapple slips were planted in spring and sampled at monthly intervals up to the green fruit stage (17 months). The concns. and amts. of N, P, and K were detd. in leaves, stems, roots, and reproductive parts. Concns. of N and K in leaves and stems reached well-defined peaks 6 months after planting, while the P concns. were minimal at about the same time. The leaves were the main region for accumulation of K; the stems had higher concns. of N. Abs. amts. of N, P, and K fell during the first 3 establishment months. In the first summer growth N and K were taken up by the plant rapidly, but P only very slowly. In the second summer all 3 elements were taken up very rapidly and considerable amts. moved into the developing fruit.

=>
=>

=> d stat que l26 nos
L1 STR
L5 1338 SEA FILE=REGISTRY SSS FUL L1
L8 STR
L9 36 SEA FILE=REGISTRY SUB=L5 SSS FUL L8
L10 37 SEA FILE=HCAPLUS ABB=ON PLU=ON L9
L12 464 SEA FILE=REGISTRY ABB=ON PLU=ON ISONITR?
L13 17185 SEA FILE=HCAPLUS ABB=ON PLU=ON L12 OR ?ISONITR?
L14 306 SEA FILE=HCAPLUS ABB=ON PLU=ON L13(L)REAGENT
L17 1686 SEA FILE=HCAPLUS ABB=ON PLU=ON L13(L)(SOLUTION OR SOLID(W)PHASE)
L18 126770 SEA FILE=HCAPLUS ABB=ON PLU=ON SYNTHE?(L)(SOLUTION OR SOLID(W)PHASE)
L19 17 SEA FILE=HCAPLUS ABB=ON PLU=ON L14 AND L17 AND L18
L20 16 SEA FILE=HCAPLUS ABB=ON PLU=ON L19 NOT L10
L22 10 SEA FILE=HCAPLUS ABB=ON PLU=ON ("PAGE PATRICK"/AU OR "PAGE PATRICK"/IN OR "PAGE PATRICK E"/AU)
L23 9 SEA FILE=HCAPLUS ABB=ON PLU=ON L22 NOT (L10 OR L20)

```
L24          57 SEA FILE=HCAPLUS ABB=ON  PLU=ON  ("PAGE P"/AU OR "PAGE P"/IN
                OR "PAGE P A"/AU OR "PAGE P B"/AU OR "PAGE P C B"/AU OR "PAGE
                P C BULMAN"/AU OR "PAGE P E"/AU OR "PAGE P J"/AU OR "PAGE P
                K"/AU OR "PAGE P R"/AU OR "PAGE P W"/AU)
L25          57 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L24 NOT (L10 OR L20 OR L23)
L26           5 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L25 AND (POLYMER? OR REAGENT
                OR ISONITRIL? OR SOLID(W)PHASE)


=>
=>

=> d ibib abs hitrn l26 1-5

L26  ANSWER 1 OF 5  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:        1996:244073  HCAPLUS
DOCUMENT NUMBER:         124:342228
TITLE:                   A new system for catalytic asymmetric oxidation of
                         sulfides using a hydrogen peroxide based
                         reagent. [Erratum to document cited in
                         CA122:80461]
AUTHOR(S):               Page, P. C. B.; Heer, J. P.; Bethell, D.;
                         Collington, E. W.; Andrews, D. M.
CORPORATE SOURCE:        Dep. Chem., Univ. Liverpool, Liverpool, L69 3BX, UK
SOURCE:                  Tetrahedron Letters (1996), 37(15), 2515
                         CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER:               Elsevier
DOCUMENT TYPE:           Journal
LANGUAGE:                English
AB   The errors were not reflected in the abstr. or the index entries.

L26  ANSWER 2 OF 5  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:        1994:681357  HCAPLUS
DOCUMENT NUMBER:         121:281357
TITLE:                   Poly(ether imide)s with hindering substituents in the
                         anhydride moiety: synthesis, properties and gas
                         permeabilities
AUTHOR(S):               Eastmond, G. C.; Page, P. C. B.; Paprotny,
                         J.; Richards, R. E.; Shaunak, R.
CORPORATE SOURCE:        Department of Chemistry, University of Liverpool,
                         Liverpool, L69 3BX, UK
SOURCE:                  Polymer (1994), 35(19), 4215-27
                         CODEN: POLMAG; ISSN: 0032-3861
DOCUMENT TYPE:           Journal
LANGUAGE:                English
AB   The synthesis of a series of bis(ether anhydrides) with hindering
     substituents, esp. tert-Bu and Me, has been developed using nucleophilic
     displacement reactions between nitrophthalonitriles and substituted
     hydroquinones, bisphenols and a naphthalene diol.  The bis(ether
     anhydrides) have been successfully incorporated into poly(ether imides)
     with hindering residues by polymn. with diamines, with and
     without alkyl substituents.  The thermal and mech. properties of a no. of
     the polymers and their permeabilities to several gases have been
     detd.  The properties of the polymers are discussed, along with
     those of related polymers.  The properties are strongly
     controlled by their structural features.  In particular, the flexibilities
     of polymer backbones and substituents influence glass transition
     temps. and, in conjunction with the influence of chain rigidity on
     packing, influence gas permeabilities and permselectivities.

L26  ANSWER 3 OF 5  HCAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:        1993:170051  HCAPLUS
DOCUMENT NUMBER:         118:170051
```

TITLE: Molecular-weight dependence of gas permeability and selectivity in copolyimides
AUTHOR(S): Eastmond, G. C.; **Page, P. C. B.**; Paprotny, J.; Richards, R. E.; Shaunak, R.
CORPORATE SOURCE: Dep. Chem., Univ. Liverpool, Liverpool, L69 3BX, UK
SOURCE: Polymer (1993), 34(3), 667-70
CODEN: POLMAG; ISSN: 0032-3861
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The gas (i.e., CO2, CH4, O, N) permeation behavior of a no. of polyimides prepd. from hexafluoroisopropylidenebis(phthalic anhydride) and equimolar mixts. of 2 diamines, including a series of copolyimides of identical structure with different mol. wts., were studied. Permeabilities and selectivities varied over a broad mol. wt. range at high mol. wts. Differences in permeability with mol. wt. were comparable to those differences achieved by modifying the chem. structures of the **polymers**.

L26 ANSWER 4 OF 5 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1992:129735 HCAPLUS
DOCUMENT NUMBER: 116:129735
TITLE: Organocuprates as initiators for methyl methacrylate **polymerization**
AUTHOR(S): Day, P.; Eastmond, G. C.; Gilchrist, T. L.; **Page, P. C. Bulman**
CORPORATE SOURCE: Dep. Chem., Univ. Liverpool, Liverpool, L69 3BX, UK
SOURCE: Journal of Macromolecular Science, Pure and Applied Chemistry (1992), A29(7), 545-56
CODEN: JSPCE6; ISSN: 1060-1325
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Lithium n-butylcyanocuprate and lithium di-n-butylcuprate were effective initiators for Me methacrylate (I) in THF; both species gave rapid **polymn**. to virtually complete conversion of monomer. PMMA polydispersities were approx. 1.5. **Polymns**. had an inherent termination reaction and a low initiator efficiency. **Polymn**. of Me vinyl ketone was virtually uncontrollable, and **polymns**. of I were inhibited by styrene.

L26 ANSWER 5 OF 5 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1975:468761 HCAPLUS
DOCUMENT NUMBER: 83:68761
TITLE: Photoelectron spectra of single crystal diacetylene **polymers**
AUTHOR(S): Bloor, D.; Stevens, G. C.; **Page, P. J.**; Williams, P. M.
CORPORATE SOURCE: Dep. Phys., Queen Mary Coll., London, UK
SOURCE: Chemical Physics Letters (1975), 33(1), 61-4
CODEN: CHPLBC; ISSN: 0009-2614
DOCUMENT TYPE: Journal
LANGUAGE: English
AB X-ray photoelectron spectra of 2 single crystal diacetylene **polymers** are reported. The obsd. and calcd. core electron binding energies are in good agreement within the limits imposed by the exptl. technique and the semiempirical calcns. employed. The uv photoelectron spectra can, in principle, provide information about the valence bands of the conjugated **polymer** chain but overlapping sidegroup bands prevented this for the materials investigated.

```
=> fil hcaplus
FILE 'HCAPLUS' ENTERED AT 11:59:13 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)
```



```
FILE COVERS 1907 - 13 Mar 2003  VOL 138 ISS 11
FILE LAST UPDATED: 12 Mar 2003  (20030312/ED)

 This file contains CAS Registry Numbers for easy and accurate
 substance identification.


=>
=>

=> d stat que nos
L1              STR
L5          1338 SEA FILE=REGISTRY SSS FUL L1
L8              STR
L9            36 SEA FILE=REGISTRY SUB=L5 SSS FUL L8
L10           37 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L9
L12          464 SEA FILE=REGISTRY ABB=ON  PLU=ON  ISONITR?
L13        17185 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L12 OR ?ISONITR?
L14          306 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)REAGENT
L17         1686 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L13(L)(SOLUTION OR SOLID(W)PHA
                 SE)
L18       126770 SEA FILE=HCAPLUS ABB=ON  PLU=ON  SYNTHE?(L)(SOLUTION OR
                 SOLID(W)PHASE)
L19           17 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L14 AND L17 AND L18
L20           16 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L19 NOT L10
L22           10 SEA FILE=HCAPLUS ABB=ON  PLU=ON  ("PAGE PATRICK"/AU OR "PAGE
                 PATRICK"/IN OR "PAGE PATRICK E"/AU)
L23            9 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L22 NOT (L10 OR L20)
L24           57 SEA FILE=HCAPLUS ABB=ON  PLU=ON  ("PAGE P"/AU OR "PAGE P"/IN
                 OR "PAGE P A"/AU OR "PAGE P B"/AU OR "PAGE P C B"/AU OR "PAGE
                 P C BULMAN"/AU OR "PAGE P E"/AU OR "PAGE P J"/AU OR "PAGE P
                 K"/AU OR "PAGE P R"/AU OR "PAGE P W"/AU)
L25           57 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L24 NOT (L10 OR L20 OR L23)
L26            5 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L25 AND (POLYMER? OR REAGENT
                 OR ISONITRIL? OR SOLID(W)PHASE)
L27         1302 SEA FILE=REGISTRY ABB=ON  PLU=ON  L5 NOT L9
L28          938 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L27
L30            5 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L28(L)REAGENT
L31            3 SEA FILE=HCAPLUS ABB=ON  PLU=ON  L30 NOT (L10 OR L20 OR L23 OR
                 L26)


=>
=>
```

=> d ibib abs hitrn l31 1-3

L31 ANSWER 1 OF 3 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2002:87580 HCAPLUS
DOCUMENT NUMBER: 136:239383
TITLE: Crystal structure of 1,3-dibenzyl-2-benzylaminothiocarbonyl-4-(4-methoxyphenyl)-1,3,4-diazaphospholidin-5-thione 4-sulfide
AUTHOR(S): Chi, Guo-Chen; Chen, Ru-Yu
CORPORATE SOURCE: Institute and National Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, Peop. Rep. China
SOURCE: Jiegou Huaxue (2002), 21(1), 31-33
CODEN: JHUADF; ISSN: 0254-5861
PUBLISHER: Jiegou Huaxue Bianji Weiyuanhui
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The title compd. crystallizes in monoclinic space group P21/n, with a 11.839(7), b 8.975(5), c 29.15(2) .ANG., .beta. 100.07(1).degree.; Z = 4, dc = 1.280; final R = 0.0434 and Rw = 0.1140 for 4787 reflections. The compd. contains a five-membered heterocycle with a P, two N and two C atoms. The five-membered ring is nearly coplanar. The P(1)-N(1) bond length (1.685 .ANG.) indicates the existence of p-d.pi. bond between N(1) and P(1) atoms.
IT **10340-91-7**, Benzylisonitrile
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with Lawesson's **reagent**)
REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L31 ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1974:95439 HCAPLUS
DOCUMENT NUMBER: 80:95439
TITLE: Isocyanides. Dissociation of metallo aldimines
AUTHOR(S): Periasamy, M. P.; Walborsky, H. M.
CORPORATE SOURCE: Dep. Chem., Florida State Univ., Tallahassee, FL, USA
SOURCE: Journal of Organic Chemistry (1974), 39(5), 611-8
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Metallo aldimines RN:C(Li)R1 were prepd. by the addition of organolithium reagents to tert-butyl isocyanide, 1,1,3,3-tetramethylbutyl isocyanide, 2-phenyl-2-butyl isocyanide, and triphenylmethyl isocyanide. The reactions of organolithium reagents, Grignard reagents, and organocopper reagents with triphenylmethyl isocyanide are discussed in detail. A new synthetic route for the formation of secondary and tertiary nitriles is described as is a simple and convenient method for the prepn. of ketones. The Li aldimines were converted to Cu aldimines by treatment with Cu2I2. Studies on the dissociative nature of metallo aldimines indicated that both relief of steric crowding (steric effect) and formation of stable intermediates (electronic effect) are the driving forces for the dissocn.
IT **1600-49-3**
RL: RCT (Reactant); RACT (Reactant or reagent)
(addn. reaction of, with Grignard **reagents** and organocopper and organolithium compds., steric effect in products from)

L31 ANSWER 3 OF 3 HCAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1972:72183 HCAPLUS
DOCUMENT NUMBER: 76:72183
TITLE: Isonitriles. Isonitrile - metal exchange reaction
AUTHOR(S): Walborsky, H. M.; Niznik, G. E.; Periasamy, M. P.
CORPORATE SOURCE: Dep. Chem., Florida State Univ., Tallahassee, FL, USA
SOURCE: Tetrahedron Letters (1971), (52), 4965-8

CODEN: TELEAY; ISSN: 0040-4039
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Ph3CNC was treated with RLi (R = Bu, sec-Bu, tert-Bu, cyclopropyl, and Ph) to give RCN and RCOR. Ph2MeCNC and sec-BuLi gave sec-BuCHO, sec-BuCN, sec-Bu2Co, and Ph2CHMe, via dissocn. of Ph2CMeN:C-(Bu-sec)Li. If R was not hindered the main product was the ketone, but tert-BuLi gave 88% tert-BuCN. At 1:2 Ph3CNCRLi, ketone yields were increased. Ph3CNC was treated with tert-BuLi and the product treated with sec-BuLi to give 83% tert-BuCOBu-sec. Also, Ph3CNC and RMgBr (R = cyclopropyl, cyclohexyl, mesityl) gave RCN (27, 78, and 39%, resp.).
IT **1600-49-3**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with organolithium **reagents**)

=> select hit rn l31 1-3
E1 THROUGH E2 ASSIGNED

=> fil reg
FILE 'REGISTRY' ENTERED AT 11:59:33 ON 13 MAR 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 12 MAR 2003 HIGHEST RN 498527-50-7
DICTIONARY FILE UPDATES: 12 MAR 2003 HIGHEST RN 498527-50-7

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

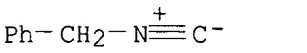
=>
=>

=> s e1-e2
1 1600-49-3/BI
(1600-49-3/RN)
1 10340-91-7/BI
(10340-91-7/RN)
L32 2 (1600-49-3/BI OR 10340-91-7/BI)

=> d ide can l32 1-2

L32 ANSWER 1 OF 2 REGISTRY COPYRIGHT 2003 ACS
RN **10340-91-7** REGISTRY
CN Benzene, (isocyanomethyl)- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzyl isocyanide (6CI, 7CI, 8CI)
OTHER NAMES:
CN (Isocyanomethyl)benzene
CN Benzyl isonitrile

FS 3D CONCORD
MF C8 H7 N
CI COM
LC STN Files: AGRICOLA, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, DETHERM*, GMELIN*, HODOC*, IFICDB, IFIPAT, IFIUDB, SPECINFO, TOXCENTER, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



355 REFERENCES IN FILE CA (1962 TO DATE)
6 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
356 REFERENCES IN FILE CAPLUS (1962 TO DATE)
13 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 138:137405

REFERENCE 2: 138:107001

REFERENCE 3: 138:75102

REFERENCE 4: 138:65539

REFERENCE 5: 138:39391

REFERENCE 6: 138:10882

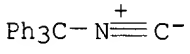
REFERENCE 7: 137:352988

REFERENCE 8: 137:337453

REFERENCE 9: 137:295253

REFERENCE 10: 137:267993

L32 ANSWER 2 OF 2 REGISTRY COPYRIGHT 2003 ACS
RN **1600-49-3** REGISTRY
CN Benzene, 1,1',1''-(isocyanomethylidyne)tris- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Trityl isocyanide (7CI)
OTHER NAMES:
CN Triphenylmethyl isocyanide
CN Trityl isonitrile
MF C20 H15 N
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS
(*File contains numerically searchable property data)



15 REFERENCES IN FILE CA (1962 TO DATE)
15 REFERENCES IN FILE CAPLUS (1962 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

REFERENCE 1: 136:401590

REFERENCE 2: 121:57086

REFERENCE 3: 114:206309

REFERENCE 4: 106:155575

REFERENCE 5: 106:101575

REFERENCE 6: 106:32184

REFERENCE 7: 95:149483

REFERENCE 8: 88:89592

REFERENCE 9: 86:154975

REFERENCE 10: 80:95439